
Evaluation of the Engineering Scale Testing of the Photo-Cat[®] Process To Treat NSCMP Rinsate Solutions

Prepared for:

Non-Stockpile Chemical Materiel
Program Manager

Contract No.: DAAM-01-96-D-0010



December, 2001

This document was prepared under contract with the United States Army for the sole purpose of evaluating the identified technology for potential application in the United States Army Chemical Demilitarization Program (CDP), based on information available to the reviewer at the time of the evaluation. Any opinions, findings, recommendations or conclusions expressed are stated in the context of the particular considerations of the CDP, and are not intended for use or reference in any way by any other party for any other purpose.

Evaluation of the Engineering Scale Testing of the Photo-Cat[®] Process To Treat NSCMP Rinsate Solutions

Prepared for:

United States Army

Non-Stockpile Chemical Materiel Program Manager

Chemical Demilitarization Project

Report No. R37-V-05

Revision 2

December, 2001

S. L. Burnham

Dr. S. Basu

C. A. Freedlund

Dr. J. M. Cardito Task Manager

Approved By: 

Stone & Webster Project Manager

Government Release By: 

NSCMP Task Manager

This document was prepared under contract with the United States Army for the sole purpose of evaluating the identified technology for potential application in the United States Army Chemical Demilitarization Program (CDP), based on information available to the reviewer at the time of the evaluation. Any opinions, findings, recommendations or conclusions expressed are stated in the context of the particular considerations of the CDP, and are not intended for use or reference in any way by any other party for any other purpose.

EXECUTIVE SUMMARY

This report evaluates the results of the Engineering Scale Tests of the Photo-Cat[®] Process. Stone & Webster, Inc. conducted these tests on behalf of Non-Stockpile Chemical Materiel Program (NSCMP) (Edward F. Doyle, Alternative Systems Demonstration and Evaluation Group Leader) to evaluate the applicability of the process to the treatment of Non-Stockpile Chemical Materiel Program (NSCMP) rinsate solutions. The tests were conducted from June 11th to June 29th, 2001, utilizing Photo-Cat[®] units located at the Purifics Facility in London, Ontario, Canada.

Test data and observations from two Work-up runs and one Validation test were completed as part of the Engineering Scale Testing of the Photo-Cat[®] process and were evaluated for each objective. Test conclusions are summarized below for each listed objective.

1. Demonstrate stable operability at maximum continuous throughput.

- Continuous stable operation of the Photo-Cat[®] unit showed destruction of greater than 99 wt% monoethanolamine (MEA) in the 2 wt% MEA rinsate simulant solution feed. In addition, it was shown that the Photo-Cat[®] unit consistently produced a final treated solution, which had less than 25 ppm TOC. In fact, the final treated solution had a TOC of 8 ppm, which represents a destruction of greater than 99 wt%.
- The 4.8 kW Photo-Cat[®] unit destroyed 328 liters of 2 wt% MEA rinsate simulant in 92.3 hours of treatment.
- Final treated liquid generated by the Photo-Cat[®] unit (treating a 2 wt% MEA rinsate simulant) should not normally be regulated as a hazardous waste and should typically require minimal, if any, pretreatment before it could be discharged to a federal wastewater treatment facility.
- Air emissions during the treatment of a 2 wt% MEA rinsate simulant from the Photo-Cat[®] system are limited to that vented from the process feed tank as the waste stream is recirculated through the treatment system. The vapor space in the storage tank is not mechanically ventilated, and instead vents limited quantities of gas primarily from gas evolution during the treatment process (CO₂, filter pulse air along with vaporized by-products). Because these flow rates were minimal (estimated at less than 4 L/min) the associated mass emissions of potential air pollutants are expected to be very low, well below thresholds triggering these permit and control technology requirements.
- No physically solid wastes were discovered in Photo-Cat[®] system during the treatment of a 2 wt% MEA rinsate simulant.

2. Demonstrate the fate of Nitrogen contained in the feed material.

- The overall material balance indicated reasonable accountability and that nearly all organic nitrogen (amine group of MEA) was converted to ammonia/ammonium which remained in the final treated liquid.

3. Provide basic engineering data to evaluate practicality for implementation in NSCMP.

- The existing mobile 4.8 kW unit should be capable of 27 gallons of rinsate per day. A 21 kW Photo-Cat[®] Unit (4'x11'x5' tall) should be capable of processing 120 gallons of 2 wt% MEA rinsate per day. Since Purifics has sold Photo-Cat units on the order of 100 kW, the proposed 21 kW unit is clearly within the practical design range.

4. Quantify and document key operating and engineering design parameters.

- The Photo-Cat[®] is a low temperature (45°C as tested) low pressure (< 50 psig) process that showed good reliability, maintainability, and operating characteristics.
- Key operating parameters including an estimated treatment rate of 960 kWhr/m³ to process 2 wt% MEA rinsate simulant to a final TOC of 25 ppm, and stoichiometric dosages of hydrogen peroxide dosage were quantified during the EST. These parameters enable the core-technology to be easily scaled for NSCMP requirements.

This document was prepared under contract with the United States Army for the sole purpose of evaluating the identified technology for potential application in the United States Army Chemical Demilitarization Program (CDP), based on information available to the reviewer at the time of the evaluation. Any opinions, findings, recommendations or conclusions expressed are stated in the context of the particular considerations of the CDP, and are not intended for use or reference in any way by any other party for any other purpose.

Based on these conclusions, it is recommended that further testing be conducted to demonstrate component destruction of actual NSCMP rinsate. The following objectives should be included in future testing:

- Characterization of final treated rinsate solution.
- Quantification of key engineering scale-up parameters such as treatment level and hydrogen peroxide dosage.
- Destruction efficiency of schedule 2 compounds.
- Characterization of gaseous emissions from the process.
- Determine sampling and analyses methods to improve on the characterization of difficult to analyze materials such as MEA.
- Applicability to other NSCMP feeds.
- Material balances – overall and for key elements.

Evaluation of the Engineering Scale Testing of the Photo-Cat[®] Process To Treat NSCMP Rinsate Solutions

TABLE OF CONTENTS

EXECUTIVE SUMMARY	i
1. Introduction	1
1.1 Objectives and Evaluation Criteria.....	1
2. Background.....	3
2.1 Technical Background.....	3
2.2 Historical Background	3
3. System Description.....	5
3.1 Batch Tank and Feed System (Figure 3-3)	6
3.2 Photocatalytic Racks (Reactor)	7
3.3 Catalyst Recovery Unit.....	8
3.4 Utilities and Support Systems.....	9
4. Test Description.....	11
4.1 Rinsate Simulant	11
4.2 Test Run Descriptions.....	11
4.2.1 Work-up Run # 1 (1.2 kW Photo-Cat [®] Unit).....	12
4.2.2 Work-up Run # 2 (4.8 kW Photo-Cat [®] Unit).....	13
4.2.3 Validation Test – (4.8 kW Photo-Cat [®] Unit).....	14
4.3 Sampling and Analysis Description	16
4.3.1 Sampling Locations	16
5. Operability	20
5.1 Batch Tank and Feed Systems	20
5.2 Photocatalytic racks	20
5.3 CRU - Pulse system	20
6. Test Results & Discussion.....	21
6.1 Liquid Characterization.....	21
6.1.1 Feed (rinsate simulant solution).....	21
6.1.2 Intermediate and Final Liquid Samples	22
6.1.3 Final Treated Liquid Disposal Evaluation.....	25
6.2 Headspace Characterization.....	27
6.2.1 Batch Tank Headspace Analysis	27
6.2.2 Air Emissions	30
6.3 TiO ₂ Slurry Analyses	31

This document was prepared under contract with the United States Army for the sole purpose of evaluating the identified technology for potential application in the United States Army Chemical Demilitarization Program (CDP), based on information available to the reviewer at the time of the evaluation. Any opinions, findings, recommendations or conclusions expressed are stated in the context of the particular considerations of the CDP, and are not intended for use or reference in any way by any other party for any other purpose.

6.4	Material Balance.....	33
6.5	NSCMP Implementation.....	33
7.	Conclusions	35
8.	Recommendations.....	36
9.	Acronyms & Abbreviations	37
10.	References	39

LIST OF TABLES

Table 1-1 Test Summary	1
Table 1-2 Test Objectives & Evaluation Criteria.....	2
Table 4-1 Rinsate Simulant Compositions.....	11
Table 4-2 Work-up Run # 1 Summary	12
Table 4-3 Work-up Run # 2 Summary	13
Table 4-4 Validation Test Summary.....	15
Table 4-5 Sample ID and Descriptions.....	16
Table 6-1 Batch Tank Liquid Samples	22
Table 6-2 Headspace Analyses	28
Table 6-3 TiO ₂ Slurry Analyses	32
Table 6-4 Material Balance	33

LIST OF FIGURES

Figure 3-1 Purifics' 4.8 kW Demonstration Photo-Cat [®] Unit.....	5
Figure 3-2 Purifics' 1.2 kW Photo-Cat [®] Test Unit.....	6
Figure 3-3 Batch Tank.....	7
Figure 3-4 Photocatalytic Racks.....	8
Figure 3-5 Catalyst Recovery Unit.....	9
Figure 3-6 Purifics Photo-Cat [®] Demonstration System – Simplified Process Flow Diagram	10
Figure 4-1 Headspace Sampling Trains	18
Figure 6-1 Power Input vs. TOC.....	23
Figure 6-2 Treated Liquid Composition	24
Figure 6-3 Acetone Concentrations	29
Figure 6-4 Headspace Ammonia vs. Treated Liquid pH	30

1. Introduction

This report evaluates the results of the Engineering Scale Tests (EST) of the Purifics Photo-Cat[®] Process. Stone & Webster, Inc. conducted these tests on behalf of the Non-Stockpile Chemical Materiel Program (NSCMP) to evaluate the applicability of the process for the treatment of NSCMP rinsate solutions.

The tests were conducted at Purifics' facility in London, Ontario, Canada, from June 11th to June 29th, 2001, utilizing a 1.2 kW Photo-Cat[®] test unit and a 4.8 kW mobile demonstration Photo-Cat[®] system. Table 1-1 summarises the test runs completed.

Table 1-1 Test Summary

Test	Work-up Runs		Validation Test
	# 1	# 2	
Test Type	Work-up	Work-up	Validation
Date	11-Jun-01	13-Jun-01	25-Jun-01 29-Jun-01
Test Unit	1.2 kW	4.8 kW	4.8 kW
Test Duration, hrs	15.8	42.75	92.3

The 1.2 kW Photo-Cat[®] test unit and the 4.8 kW mobile demonstration Photo-Cat[®] unit was set-up in the workshop area of Purifics' facility. Purifics performed the tests under a subcontract to Stone & Webster, Inc. on behalf of the NSCMP under their Program and Integration Support Contract. Stone & Webster subcontracted TRC Environmental Corporation for independent sampling and analytical services in support of the testing.

The objectives of the EST and the Evaluation Criteria for the objectives to evaluate the test's performance are given below. Section 2 of this report provides a summary of Stone & Webster's technology evaluation efforts and the Photo-Cat[®] process. Section 3 describes the Photo-Cat[®] demonstration unit tested. Section 4 describes the test runs completed as part of the EST. The results of the tests are presented in Sections 5 and 6. Section 5 includes a discussion of the operability of the Photo-Cat[®]. Section 6 presents the analytical results of the samples collected during testing. Sections 7 and 8 present the test conclusions and recommendations for path forward.

1.1 Objectives and Evaluation Criteria

The overall objective is to perform testing to determine the applicability of the Photo-Cat[®] system to treat NSCMP MEA-based rinsate solutions. The proposed test was appropriately designed to provide results, which will allow determination as to whether the specific test objectives have been met.

Table 1-2 lists the specific test objectives coupled with the evaluation criteria for each objective.

Table 1-2 Test Objectives & Evaluation Criteria

Test Objective	Evaluation Criteria
1. Demonstrate stable operability of the Photo-Cat [®] system at or near maximum destruction rate for a rinsate simulant material.	<ul style="list-style-type: none"> Continuous stable operation with all systems controlled and no system function overridden for the duration of the tests. Target destruction efficiency of at least 99% with less than 25 ppm TOC in liquid effluent Liquid effluents meet limits for disposal from Federal Wastewater Treatment Facility Solid residuals can be disposed of at RCRA facility Gaseous effluents are permissible
2. Determine the fate of nitrogen contained in the feed material during operation of the Photo-Cat [®] System.	<ul style="list-style-type: none"> Material balance closure for nitrogen. Overall material balance for process unit
3. Provide basic engineering data to evaluate the Photo-Cat [®] System practicality for implementation in the NSCM Program	<ul style="list-style-type: none"> System operating characteristics System safety including engineered safeguards Reliability, availability and maintainability Ability to obtain a permit for the process
4. Quantify and document key operating and engineering design parameters to support conceptual design package	<ul style="list-style-type: none"> Documentation of key operating parameters, critical scale-up parameters and core technology scale-up philosophies which support conceptual design packages

2. BACKGROUND

2.1 Technical Background

Photo-Cat[®], developed by Purifics[®] Environmental Technologies Inc. (Purifics[®]) of London, Ontario, is a Photocatalytic Oxidation water treatment process to detoxify/purify water of organic contaminants. The primary features of the Photo-Cat[®] system are its ultraviolet (UV) lamps, hydrogen peroxide chemical handling equipment, and recirculation of titanium dioxide (TiO₂) catalyst through the UV reactor in the feed / product stream. The TiO₂ and UV light catalyze the effect of hydrogen peroxide in the oxidation of chemical bonds in the organic materials (Purifics' website www.purifics.com contains descriptions and illustrations of reaction mechanisms).

Photo-Cat[®] has experience treating hydrocarbons, chlorinated hydrocarbons and energetics. Purifics does not have experience treating chemical agents, however it has successfully demonstrated destruction of similar type compounds¹.

Photo-Cat[®] is a treatment process for destroying organic contamination in water. Influent concentrations can range from ppm to 3% TOC². At this time, there are over a dozen industrial installations using the Photo-Cat[®] system and operating under permits from a variety of state and federal regulatory agencies. Purifics[®] offers pilot scale testing using its mobile systems for short term on site testing and/or treatment.

Purifics[®] claims that the advantages of the Photo-Cat[®] process over traditional UV/Ox systems, are: lower operating and maintenance costs; no fouling of quartz tubes (therefore, no wiper mechanisms are required); and the ability to treat wastewater streams with suspended oil, turbidity and high levels of total dissolved solids.

2.2 Historical Background

The U.S. Army Program Manager for Chemical Demilitarization (PMCD) established the Non-Stockpile Chemical Materiel Program (NSCMP) with the mission to provide centralized management and direction to the Department of Defense for the disposal of non-stockpile chemical materiel in a safe, environmentally sound and cost effective manner. The NSCMP includes five categories of chemical warfare materiel (CWM): binary chemical weapons; former production facilities; miscellaneous CWM; recovered chemical weapons; and buried CWM. Substantial differences exist between CWM in the Stockpile and Non-Stockpile programs. Whereas the stockpiled CWM is present in larger quantities, non-stockpile CWM encompasses a greater variety of materiel with far more physical configurations and agent-fill types. The variety, locations and deteriorated physical condition of non-stockpile CWM pose unique requirements for treatment systems.

To support accomplishment of its mission, the NSCMP developed an Overarching Research Plan (ORP) which establishes the goals, requirements, and approaches for evaluating and developing technologies for the safe and efficient disposal of non-stockpile CWM. The ORP identifies systems that NSCMP has and is continuing to develop to meet its mission goals. The ORP also identifies additional needs and associated schedule to support accomplishment of these goals.

To meet these needs, NSCMP has identified several additional systems for application to non-stockpile CWM based on the results of technology evaluations and

This document was prepared under contract with the United States Army for the sole purpose of evaluating the identified technology for potential application in the United States Army Chemical Demilitarization Program (CDP), based on information available to the reviewer at the time of the evaluation. Any opinions, findings, recommendations or conclusions expressed are stated in the context of the particular considerations of the CDP, and are not intended for use or reference in any way by any other party for any other purpose.

demonstration testing performed as part of the PMCD Alternative Technologies and Approaches Program (ATAP) and the Assembled Chemical Weapons Assessment Program (ACWAP). To meet the ORP goals, NSCMP has determined that engineering design data is required to support full-scale implementation of CWM treatment systems. NSCMP (Edward F. Doyle, Alternative Systems Demonstration and Evaluation Group Leader) identified UV Oxidation as one of the technologies for which engineering design studies are to be performed to support full-scale implementation.

3. SYSTEM DESCRIPTION

The Engineering Scale Testing of the Photo-Cat[®] Process to treat NSCMP rinsate solutions was performed utilizing both a 1.2 kW Photo-Cat[®] test unit and the 4.8 kW mobile demonstration Photo-Cat[®] unit which were located at the Purifics facility in London, Ontario, Canada. The 4.8 kW mobile unit, which has been used to demonstrate the destruction of organic wastes, is housed in an 18' trailer shown in Figure 3-1. Figure 3-2 shows the skid-mounted 1.2 kW unit located in the facility. The 4.8 kW Photo-Cat[®] System tested consisted of the four main systems.

- Batch feed system
- Photocatalytic racks
- Catalyst recovery unit
- Utilities & Support Systems (not shown on Process Flow Diagram - PFD)

The processing systems are shown on the simplified Process Flow Diagram (Figure 3-6) and are discussed below:

Figure 3-1 Purifics' 4.8 kW Demonstration Photo-Cat[®] Unit



Figure 3-2 Purifics' 1.2 kW Photo-Cat[®] Test Unit

3.1 Batch Tank and Feed System (Figure 3-3)

The polyethylene batch tank used for the 4.8 kW unit has a nominal volume 1 m³. The solution to be treated is initially charged to the batch tank through the top manway. The tank has a small ¼" top vent to atmosphere, a ¼" side nozzle for headspace sampling, a ¾" bottom nozzle and a ¾" side nozzle for solution circulation. A variable frequency motor driven circulation pump (316 SS) draws liquid from the bottom nozzle of the batch tank and feeds liquid to the photocatalytic racks. The flow rate of the liquid through the pump is monitored by a flow indicator that sends a signal to the Program Logic Controller / Supervisory Control And Data Acquisition (PLC/SCADA) where it is compared with a set point. The flow rate can be set between 4 to 30 liters per minute. The liquid returning to the batch tank from the photocatalytic unit is discharged to the batch tank through the side nozzle.

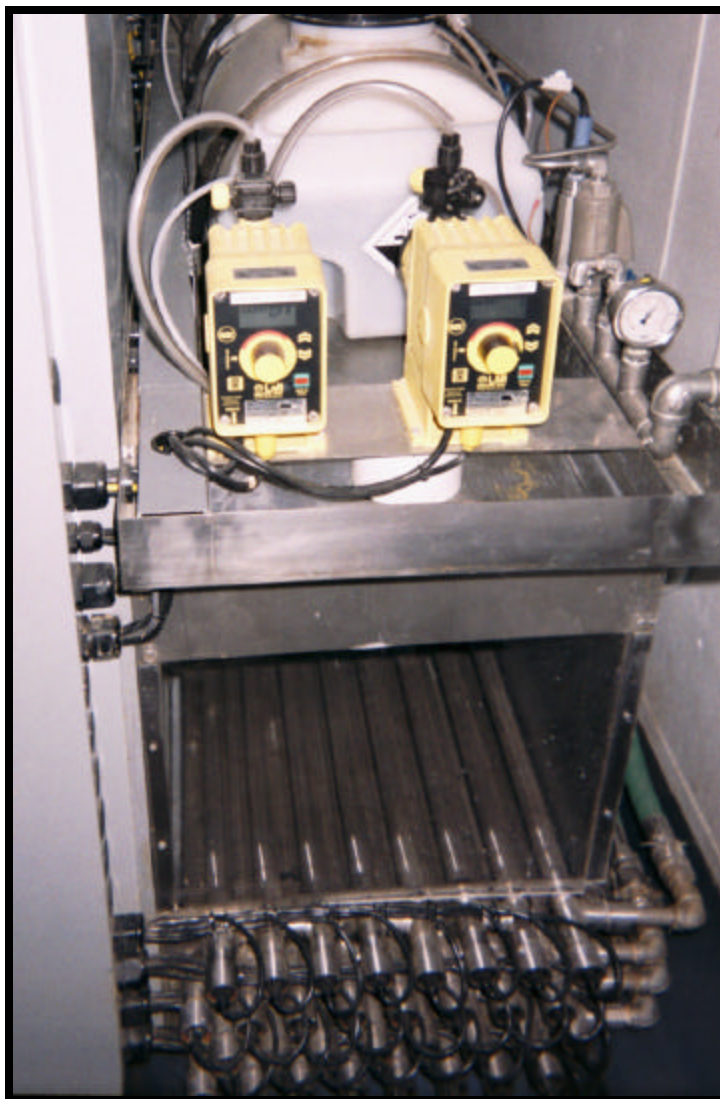
The liquid from the circulation pump flows to the 4.8 kW Photo-Cat[®] processing unit where 35 wt% peroxide can be injected from the peroxide feed pump. The hydrogen peroxide is stored in a cylindrical tote tank and inserted into a secondary containment cylinder. In addition, 93 wt% sulfuric acid can be injected to control the pH of process stream to the photocatalytic racks. The peroxide and sulfuric acid feed pumps are diaphragm metering pumps that are controlled via the PLC/SCADA system. Following the peroxide and sulfuric addition, the treated liquid flows through a static mixer and is combined with the titanium dioxide slurry which is recycled from the Catalyst Recovery Unit (CRU – see Section 3.3).

Figure 3-3 Batch Tank

3.2 Photocatalytic Racks (Reactor)

The fluid to be treated along with hydrogen peroxide and TiO_2 slurry are passed through the photocatalytic racks (2 racks with 16 tubes per rack) in series where the titanium dioxide is activated with UV light to generate oxidation and reduction reactions with the organic contaminants in the water. Each tube is made of 316 stainless steel, 10' in length and house two 5-foot long standard germicidal G64T5 lamps (254 nm) which can be serviced on either end of the rack. Each lamp has an input power of 75W and is nominally 39% efficient³. See Figure 3-4 which shows the photocatalytic racks of the 4.8 kW unit. The UV lamps are separated from the process fluid by a quartz tube that is mechanically sealed to the stainless steel tube. The process fluid flows in the annular space between the quartz tubes and the surrounding metal tubes. The photocatalytic racks are cooled by a fan that draws ambient air across the racks and discharges through the roof of the trailer.

This document was prepared under contract with the United States Army for the sole purpose of evaluating the identified technology for potential application in the United States Army Chemical Demilitarization Program (CDP), based on information available to the reviewer at the time of the evaluation. Any opinions, findings, recommendations or conclusions expressed are stated in the context of the particular considerations of the CDP, and are not intended for use or reference in any way by any other party for any other purpose.

Figure 3-4 Photocatalytic Racks

3.3 Catalyst Recovery Unit

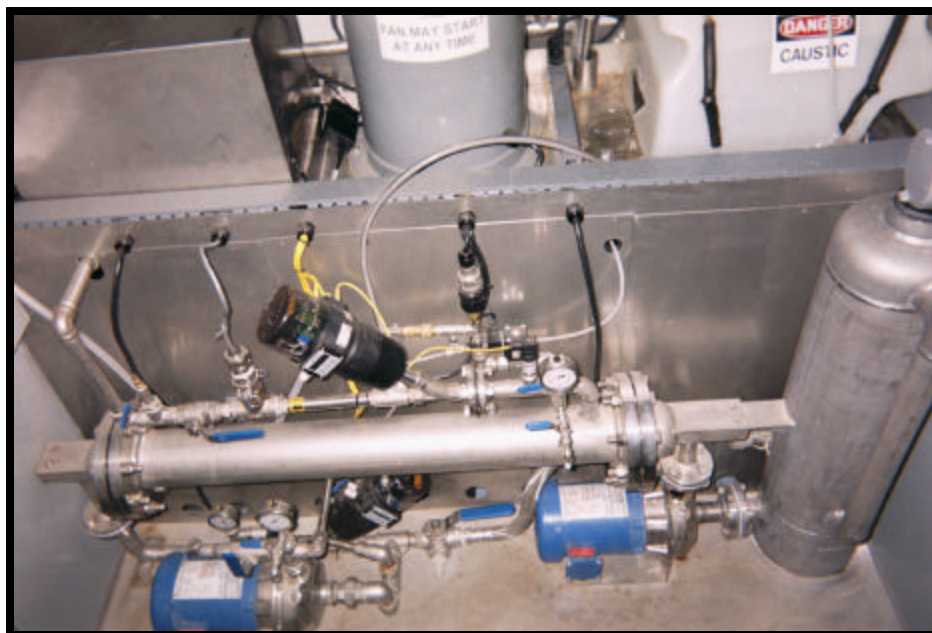
Slurry exiting the photocatalytic racks passes into the Slurry Accumulator (316 SS). The slurry from the slurry accumulator is pumped via the Slurry Accumulator Pump to the Catalyst Recovery Unit (CRU – see Figure 3-5) where the catalyst is continuously recovered with a sub-micron ceramic filter. The filtrate (liquid phase) passes through the ceramic filter and is discharged to the batch tank. The catalyst along with residual liquid passes through a control valve (CV-1 – see Figure 3-6) and to the slurry injection pump where the concentrated slurry is injected back into the process fluid upstream of the photocatalytic racks.

In order to keep the ceramic filter from plugging with catalyst solids, the CRU is periodically (once per minute) pulsed with compressed air (approximately 80 psig for $\frac{1}{4}$ second duration). Prior to the pulse, the control valve (CV-2 – see Figure 3-6) on the line returning process fluid to the batch tank is closed. A solenoid valve on the compressed air line upstream of CV-2 is quickly opened and then closed

(approximately ¼ second duration). The back flow pulse created by the compressed air dislodges solids from the ceramic filter and allows them to flow to the Slurry Injection Pump. CV-1 is then opened allowing the liquid along with the air from the pulse to pass into the batch tank. The pulse sequence of valve openings and closings are controlled by the PLC/SCADA system. The air entering the batch tank from the pulse exits the tank through the top vent.

Prior to returning liquid to the batch tank, caustic solution can be injected to control the pH of the returning flow as required. Caustic injection is accomplished using a positive displacement Caustic Feed Pump which flows into the return line upstream of a static mixer and pH probe. The PLC controls the caustic feed pump to meet a set point entered into the control system. No caustic was used for these tests.

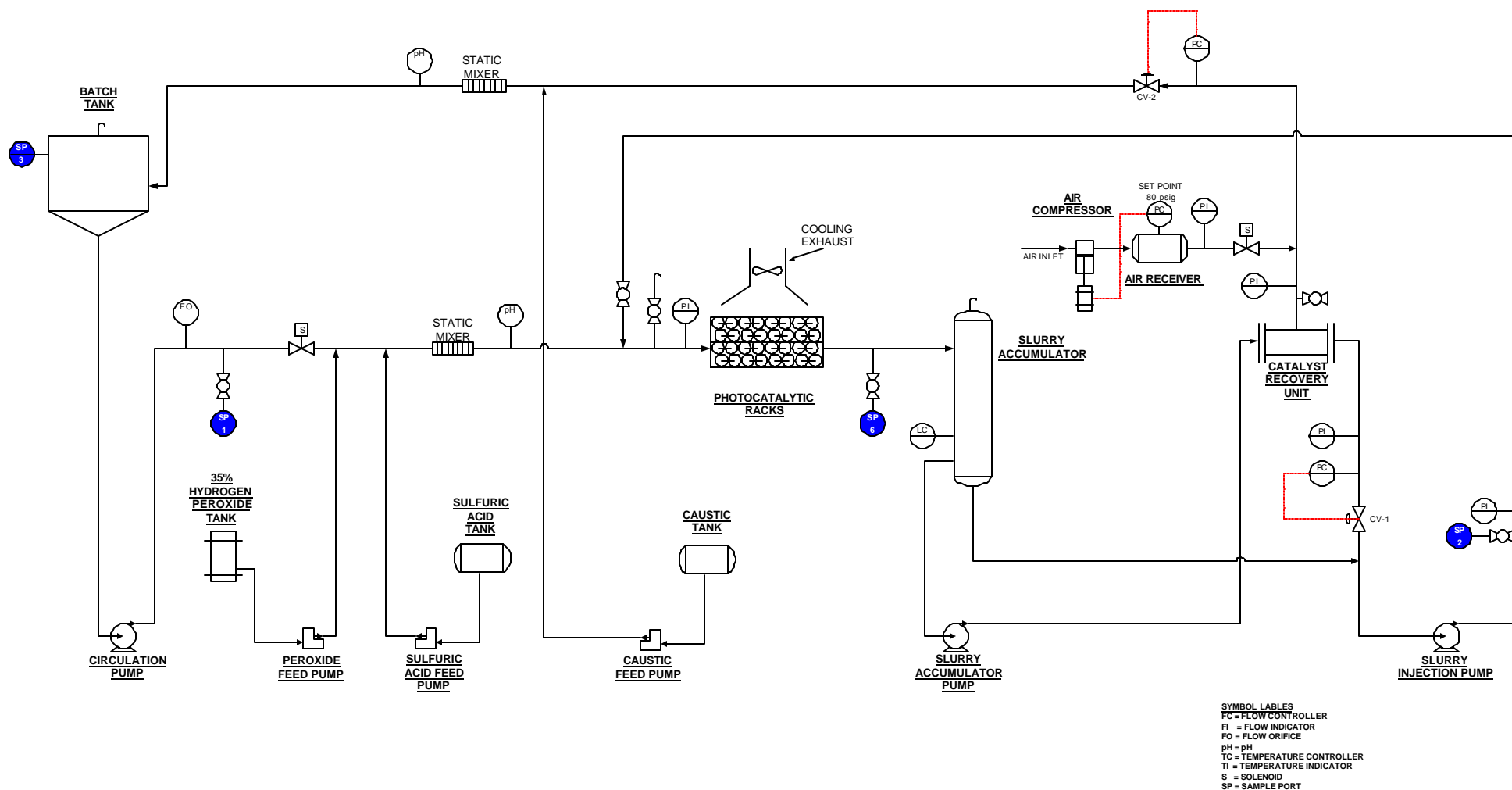
Figure 3-5 Catalyst Recovery Unit



3.4 Utilities and Support Systems

The mobile treatment system was supplied with a 230V, 3 phase, 4 wire power supply fused for 30 amps. This powered the process pumps, UV lights and control system. In addition, a single 110V – 15 amp power source was required to operate miscellaneous equipment including lights in the trailer and the air compressor. An air compressor with a regulator and a 3 gallon receiver supplied all the air requirements for the unit. No equipment was designed to use cooling water for any reason.

All monitoring is performed through the Photo-Cat's a WonderWare SCADA system. The SCADA is a man-machine interface for the PLC, and allows the operator to monitor and control the system. Routine system checks can be performed in order to ensure system integrity.

Figure 3-6 Purifics Photo-Cat[®] Demonstration System – Simplified Process Flow Diagram

This document was prepared under contract with the United States Army for the sole purpose of evaluating the identified technology for potential application in the United States Army Chemical Demilitarization Program (CDP), based on information available to the reviewer at the time of the evaluation. Any opinions, findings, recommendations or conclusions expressed are stated in the context of the particular considerations of the CDP, and are not intended for use or reference in any way by any other party for any other purpose.

4. TEST DESCRIPTION

This section presents descriptions of the Photo-Cat[®] tests conducted during June of 2001. The test descriptions include a discussion of the rinsate simulant, descriptions of each test run, and the sampling and analyses conducted.

4.1 Rinsate Simulant

The rinsate used for the validation testing was a 2 wt% MEA solution in water. Seven rinsates generated from the destruction of M139 bomblets (containing GB-Sarin) in the Explosive Destruction System (EDS) generally had concentrations between 1 to 2 wt% MEA⁴. Assuming a concentration of 2 wt% MEA in the rinsates, estimates for other components in the rinsates were generated by using the MEA concentration as a ratio based on neutralent concentrations from monoethanolamine (MEA)-based Munitions Management Device (MMD) neutralents.⁵ This resulted in a general NSCMP rinsate simulant as shown in Table 4-1.

Table 4-1 Rinsate Simulant Compositions

Agent Neutralents Rinsates	NSCMP RINSATE			RINSATE SIMULANT		
	Major Components	Chemical Formula	Wt% in Rinsate ¹	Equivalent component in Simulant	Chemical Formula	Wt% in Simulant
HD (distilled sulfur mustard) Neutralent rinsate	MEA	C ₂ H ₇ NO	2.00	MEA	C ₂ H ₇ NO	2.0
	Water	H ₂ O	97.68	Water	H ₂ O	98.0
	MEA HCl	C ₂ H ₆ ON Cl	0.19			
	HETM	C ₆ H ₁₃ NOS	0.13			
	TOTAL		100.00			100.0
GB (sarin) Neutralent rinsate	MEA	C ₂ H ₇ NO	2.00	MEA	C ₂ H ₇ NO	2.0
	Water	H ₂ O	97.37	Water	H ₂ O	98.0
	MEA IMP	C ₄ H ₁₀ O ₃ P	0.26			
	MEA HF	C ₂ H ₆ ON F	0.21			
	GB MEA	C ₆ H ₁₅ NO ₃ P	0.16			
	TOTAL		100.00			100.0

Assumptions

1) Percentages for rinsates were based on a 2 wt% MEA rinsate concentration and estimated other components based on MEA wt% from neutralents compositions taken from MMD-1 RD&D, RCRA Permit Application, Attachment 4, Appendix A, page 6. An average value within the quoted range was chosen.

4.2 Test Run Descriptions

The Engineering Scale Testing of the Photo-Cat[®] process consisted of two work-up runs using the 1.2 kW Photo-Cat[®] test unit and the 4.8 kW demonstration Photo-Cat[®] unit, and one validation run using only the 4.8 kW demonstration Photo-Cat[®] unit at the Purifies facility in London, Ontario, Canada.

4.2.1 Work-up Run # 1 (1.2 kW Photo-Cat[®] Unit)

The key objectives of the work-up runs were to obtain the required treatment time, power input, and required hydrogen peroxide to meet the treatment specification of less than 25 ppm Total Organic Carbon (TOC) in the treated liquid (i.e., obtain the power per treated volume – kWh/m³ ratio at specification). The key monitoring variable for this Work-up Run was TOC, which was measured using a Hach TOC test kit. Samples for laboratory analyses were not collected or planned for the Work-up Runs.

Work-up Run # 1 was performed in the 1.2 kW Photo-Cat[®] test unit located at the Purifics facility in London, Ontario, Canada. The test reactor draws up to 5 amps at 240 volts, or 1.2 kW. Since the power input is fixed at 1.2 kW, operating time (or batch time) and hydrogen peroxide dosage rate are the only remaining variables. The pH of the test solution was monitored on-line and logged, both upstream and downstream of the Photo-Cat[®] reactor.

The batch tank for the 1.2 kW unit was charged with 39 Liters of 0.5 wt% MEA solution (1970 ppm theoretical total organic carbon). The MEA was mixed directly with tap water by pouring the MEA directly into the water in the batch tank. The feed pump was used to circulate the solution through the Photo-Cat[®] unit (no UV lights on) and back to the batch tank to mix the solution. Prior to tuning on the UV lights, a sample of the initial solution was drawn and analyzed for TOC. The initial TOC measured (1284 ppm) was less than expected (1970 ppm). Purifics attributes the discrepancy to incomplete mixing/dissolving prior to sample collection (see Section 4.2.3 for resolution to mixing problem). A summary of Work-up Run #1 is shown in Table 4-2.

Table 4-2 Work-up Run # 1 Summary

Run Time [Hours]	System Volume [L]	Photo-Cat [®] Power [kW]	Treatment Ratio [kWhr/m ³]	TOC in Batch Tank [ppm]	TOC Removal [%]	TOC Removal Rate [mg/kWh]
0.0	39	1.2	0	1284	0.0	-
1.0	39	1.2	31	1212	5.6	72.0
2.0	39	1.2	62	1132	11.8	80.0
5.5	39	1.2	169	924	28.0	59.4
8.0	39	1.2	246	439	65.8	194.0
9.0	39	1.2	277	317	75.3	122.0
10.5	39	1.2	323	239	81.4	52.0
11.5	39	1.2	354	174	86.4	65.0
12.8	39	1.2	394	151	88.2	17.7
14.3	39	1.2	440	125	90.3	17.3
15.8	39	1.2	486	25	98.1	66.7

Notes:

- (1) Initial MEA concentration 0.5 wt%.

The results suggest that a 0.5 wt% MEA solution could be treated to less than 25 ppm TOC with a 486 kWhr/m³ treatment rate. During the test, Purifics

measured residual hydrogen peroxide concentrations in the treated liquid. Purifics indicated that there were times that no residual hydrogen peroxide was determined, which suggested that the Photo-Cat[®] system was starved of oxygen and further improvements could be accomplished with additional hydrogen peroxide.

4.2.2 Work-up Run # 2 (4.8 kW Photo-Cat[®] Unit)

Following Work-up Run # 1, Work-up Run # 2 was conducted in the demonstration 4.8 kW Photo-Cat[®] test unit located at the Purifics facility in London, Ontario, Canada. The test reactor draws up to 20 amps at 240 volts, or 4.8 kW. Since the power output is fixed at 4.8 kW, operating time (or batch time) and hydrogen peroxide dosage rate are the only remaining variables. The pH of the test solution was monitored on-line and logged, both upstream and downstream of the Photo-Cat[®] reactor.

The 1 m³ batch tank used for the 4.8 kW unit was charged with 130 Liters of 2.0 wt% MEA solution (7865 ppm theoretical). The MEA was mixed with tap water by pouring the MEA directly into the water in the batch tank. The feed pump was used to circulate the solution through the Photo-Cat[®] unit (no UV lights on) and back to the batch tank to mix the solution. Prior to turning on the UV lights, a sample of the initial solution was drawn and analyzed for TOC that resulted in a concentration of 4560 ppm TOC. The initial TOC measured (4560 ppm) was less than expected (7865 ppm). In fact, after 2.8 hours of treatment, the TOC was measured at 4710 ppm, which was greater than the initial TOC measurement. Purifics attributes the discrepancy to incomplete mixing/dissolving prior to sample collection (see Section 4.2.3 for resolution to mixing problem). A summary of Work-up Run #2 is shown in Table 4-3.

Table 4-3 Work-up Run # 2 Summary

Run Time [Hours]	System Volume ¹ [L]	Photo-Cat [®] Power [kW]	Treatment Ratio [kWhr/m ³]	TOC in Batch Tank [ppm]	TOC Removal [%]	TOC Removal Rate [mg/kWh]
0.0	130	4.8	0	4560	0.0	-
2.8	130	4.8	102	4710	-3.3	-54.5
6.3	130	4.8	231	3600	21.1	317.1
21.0	130	4.8	775	1350	70.4	152.5
26.3	130	4.8	969	502	89.0	161.5
29.7	130	4.8	1097	318	93.0	53.3
42.8	130	4.8	1578	30	99.3	22.1

Notes:

(1) Initial MEA concentration 2.0 wt%.

The results suggest that a 2.0 wt% MEA solution could be treated to less than 30 ppm TOC with a 1578 kWhr/m³ treatment rate. During the test, Purifics measured residual hydrogen peroxide concentrations in the treated liquid. Purifics indicated that there were times that no residual hydrogen peroxide was

determined, which suggested that the Photo-Cat[®] system was starved of oxygen and further improvements could be accomplished with additional hydrogen peroxide.

Work-up run # 2 had four times the organic loading (using theoretical loading based on amount of MEA added to system) as Work-up Run # 1 but had a treatment ratio that was approximately 3.24 times greater. Purifics explained that this discrepancy is due to the increased frequency in which Work-up Run # 1 was starved for oxygen (hydrogen peroxide) when compared to Work-up Run # 2. Purifics also concluded that the hydrogen peroxide requirements for the Photo-Cat[®] were approximately 10% greater than the stoichiometric requirements⁶.

4.2.3 Validation Test – (4.8 kW Photo-Cat[®] Unit)

The Validation Test was conducted in the demonstration 4.8 kW Photo-Cat[®] unit. The test plan for the validation testing had a treatment duration of 100 hours. The calculation of the volume of solution to be treated was based on the results from Work-up Run # 2 (approximately 1580 kWh/m³ of treatment to reduce a 2 wt% MEA to 25 ppm TOC). During a 100 hour test, the 4.8 kW Photo-Cat[®] unit was estimated to be able to treat 328 L of 2 wt% MEA to less than 25 ppm TOC. Note that the calculation of the treatment volume is complicated by taking into account the volume of treated solution removed from the system for scheduled sampling activities. The stoichiometric hydrogen peroxide requirement for a 328L batch of 2% MEA solution is 61.7 L of 35% H₂O₂.⁷

In order to avoid the MEA mixing/dissolving problems suspected in the work-up runs, Purifics decided to mix/dissolve the MEA in a small batch of warm water before adding to the batch tank. A summary of the 2 wt% MEA solution preparation is as follows:

1. Add 300 liters of tap water to 1 m³ batch tank.
2. Circulate water from batch tank through the Photo-Cat[®] unit for 2 hours.
3. Add 6.495 liters of MEA to a mixing jug.
4. Add warm water to mixing jug until a solution volume of 28 liters is obtained.
5. Mix solution in mixing jug until all MEA is dissolved.
6. Add MEA solution from mixing jug to 1 m³ batch tank.
7. Circulate MEA solution through Photo-Cat[®] unit for 2 hours.
8. Add sulfuric acid solution with the Photo-Cat's automated acidification system to the system to bring the circulation solution from a basic condition to a pH of 7.

Purifics felt that lowering the pH of the initial MEA solutions from 11.4 to 7 would minimize the amount of ammonia that could build up in the headspace of the batch tank during treatment and therefore minimize the possible emissions of ammonia from the batch tank.

At 1130 hrs, June 25, 2001, with the system circulating the MEA solution at 15 L/min and 75 g of TiO₂ charged to the slurry tank, the UV lights on the Photo-Cat[®] system were turned on marking the beginning of the validation test. A summary of the validation test is shown in Table 4-4.

This document was prepared under contract with the United States Army for the sole purpose of evaluating the identified technology for potential application in the United States Army Chemical Demilitarization Program (CDP), based on information available to the reviewer at the time of the evaluation. Any opinions, findings, recommendations or conclusions expressed are stated in the context of the particular considerations of the CDP, and are not intended for use or reference in any way by any other party for any other purpose.

Table 4-4 Validation Test Summary

Run Time [Hours]	System Volume [L]	Photo-Cat® Power [kW]	Treatment Ratio [kWhr/m ³]	Peroxide Dosage (35 wt%) [L/min]	TOC ² in Batch Tank [ppm]	TOC Removal [%]	TOC Removal Rate [mg/kWh]
0.0	318.9	4.8	0	NA	8000	0.0	-
3.5	317.0	4.8	53	NA	7300	8.8	200.0
9.8	317.5	4.8	149	NA	6900	13.8	63.2
21.3	321.9	4.8	318	NA	5300	33.8	139.1
29.3	323.6	4.8	435	NA	4100	48.8	150.0
44.3	330.6	4.8	644	NA	1300	83.8	186.7
52.0	332.1	4.8	752	NA	530	93.4	100.4
68.7	340.3	4.8	969	NA	20	99.8	30.6
76.8	342.1	4.8	1077	NA	11	99.9	1.1
92.3	349.0	4.8	1270	NA	8.1	99.9	0.2
92.5	344.7	4.8	1288	NA	7.9	99.9	1.2

Notes:

- (1) Initial MEA concentration 2.0 wt%.
- (2) Laboratory analyses results.
- (3) 55 liters of 35 wt% hydrogen peroxide was added during the first 59 hours of treatment.
13 additional liters of hydrogen peroxide was added during the last 33 hours of treatment.
- (4) Circulation flow rate was set at 15 L/min for duration of test.

Based on the initial measurement of TOC in the batch tank of 8000 ppm vs. the 7865 ppm TOC expected theoretically, the new mixing/dissolving method proved successful. The results suggest that a 2.0 wt% MEA solution could be treated to less than 25 ppm TOC with a 960 kWhr/m³ treatment rate. During the validation test, Purifics adjusted the flow rate of hydrogen peroxide to the Photo-Cat® unit. A higher flow rate of hydrogen peroxide was utilized for the first 838 kWhr/m³ of treatment, which totaled an estimated 55 Liters of 35 wt% hydrogen peroxide. The remaining 13 L of 35 wt% hydrogen peroxide was added in the following 433 kWhr/m³ of treatment. Further data on hydrogen peroxide dosage and residual is pending.

The temperatures of the treated solution ranged between 45 and 48°C. Purifics recommends that the temperature of the solution should be below 35°C to maintain full UV output. The increased temperatures were caused by inadequate cooling fan capacity for batch operation. UV output can decrease slightly when temperatures exceed 40°C⁸, however the impact on the treatment rate with the higher operating temperatures is small.

The test plan specified sampling and analysis of liquid, solid, and gaseous streams from the validation run. Stone & Webster subcontracted the sampling services to TRC Environmental Corporation. In addition, Purifics periodically took samples of the treated liquid and analyzed them in-house for TOC. The in-house TOC analyses were necessary to ascertain the rate of progress of the catalyzed oxidation prior to actual laboratory results.

This document was prepared under contract with the United States Army for the sole purpose of evaluating the identified technology for potential application in the United States Army Chemical Demilitarization Program (CDP), based on information available to the reviewer at the time of the evaluation. Any opinions, findings, recommendations or conclusions expressed are stated in the context of the particular considerations of the CDP, and are not intended for use or reference in any way by any other party for any other purpose.

4.3 Sampling and Analysis Description

The Sampling and Analysis activities were under the supervision of TRC. Their subcontract entailed oversight of the sample collection, transport of the samples to the respective laboratories, Quality Control/Quality Assurance associated with these tasks and reporting of the results. Philip Analytical (Ontario, Canada) was subcontracted by TRC to carry out all required analyses.

The Purifics personnel at the test facility were responsible for collection of system operating data such as temperature and pH of the feed and the discharge streams as well as the temperature and pressure in the Batch Tank. Purifics also carried out preliminary TOC tests to aid the operation of the process. TRC personnel were responsible for all other sampling activities, while Purifics personnel were responsible for the collection of monitoring information and coordination and timing of sampling activities.

The Sampling and Analysis Plan (SAP) prepared by Purifics and TRC for this test program specified the collection of samples identified in Table 4-5. The location of specific sample points are shown in Figure 3-6.

Table 4-5 Sample ID and Descriptions

Sample ID	Sample Description
SP-1	Feed to Photocatalytic Racks
SP-2	Slurry Injection. No samples taken.
SP-3	Head Space of Batch Tank
SP-4	Liquid in Batch Tank. No samples taken.
SP-5	Solids from Batch Tank. No samples due to lack of solids.
SP-6	Photocatalytic Rack discharge with Slurry

4.3.1 Sampling Locations

Six sampling locations were identified for collecting representative samples of the feed, process, and effluents.

4.3.1.1 SP-1 – Feed to Photocatalytic Racks

The feed stream samples (SP-1) were normally scheduled to be taken twice a day. These liquid samples were taken down stream of the Circulation Pump. The following parameters were scheduled for analysis:

- Ammonia
- Alcohols (methanol, ethanol)
- Aldehydes/Ketones
- Cyanides/Cyanates/Thiocyanates

- Nitrate/Nitrite Ions
- Nitrogen – TKN (Total Kjeldahl Nitrogen) & TON (Total Organic Nitrogen)
- Organic Acids (C1-C4)
- COD (Chemical Oxygen Demand)
- TSS (Total Suspended Solids)
- VOCs (Volatile Organic Compounds)
- SVOCs (Semi-Volatile Organic Compounds)
- Al, Cr, Cu, Fe, Hg, Zn
- Total Titanium (Ti)
- Total Organic Carbon (TOC), Total Inorganic Carbon (TIC)
- MEA (Monoethanolamine)
- Sulfate

4.3.1.2 *SP-2 – Slurry Injection*

Sample location was identified in SAP but no analyses were performed because sample would be essentially identical to SP-6.

4.3.1.3 *SP-3 – Headspace of Batch Tank*

Headspace samples of the batch tank were taken once a day and were taken through a vent located on the side of the batch tank. Figure 4-1 shows the headspace sampling system.

Figure 4-1 Headspace Sampling Trains

The following parameters were collected for analyses:

- VOCs, O₂, CO₂, CO, H₂, N₂, THC (Total Hydrocarbons) (Method TO-15)
- SVOCs (SW-846 Method 0010)
- HCN/NH₃ (SW-846 Method 0050)
- NO_x (SW-846 Method 7D)
- MEA (NIOSH Method 2007)

4.3.1.4 SP-4 – Liquid in Batch Tank

This sample is identical to sample location SP-1 and was not used.

4.3.1.5 SP-5 – Solids from Batch Tank

If solids were formed during the process, samples of the solids would be analyzed. No solids were discovered therefore no samples were taken.

4.3.1.6 SP-6 – Photocatalytic Rack discharge with Slurry

Samples were taken from the discharge of the photocatalytic racks that contained the TiO₂ slurry. The sample point is located between the Photocatalytic Racks and the Slurry Accumulator. The following analyses were carried out:

- Ammonia
- Alcohols (methanol, ethanol)
- Aldehydes/Ketones
- Cyanides/Cyanates/Thiocyanates
- Nitrate/Nitrite Ions
- Nitrogen (TKN & TON)
- Organic Acids (C1-C4)
- COD
- TSS (Total Suspended Solids)
- VOCs (Volatile Organic Compounds)
- SVOCs (Semi-Volatile Organic Compounds)
- Al, Cr, Cu, Fe, Hg, Zn
- Total Titanium (Ti)
- Total Organic Carbon (TOC), Total Inorganic Carbon (TIC)
- MEA (Monoethanolamine)
- Sulfate

5. OPERABILITY

This section presents Stone & Webster's comments on the design and operation of the Purifics demonstration 4.8 kW Photo-Cat[®] unit observed during the Engineering Scale Testing. Comments on the operation of the major equipment items and as well as observations on operational modes (with recommendations for modification), standard operating procedures, process safety and worker safety are provided.

The operations of the following subsystems were observed and are evaluated.

5.1 Batch Tank and Feed Systems

During the operation of the 4.8 kW demonstration Photo-Cat[®] unit, the circulation pump was observed to be leaking small amounts of process fluid. The source of the leak was not determined nor was the leak significant enough to stop the validation test. It is recommended that the seal type and materials of construction of this pump be reviewed prior to operations which process feeds consistent with NSCMP rinsates.

5.2 Photocatalytic racks

During the operation of the 4.8 kW demonstration Photo-Cat[®] unit, the photocatalytic racks (316 stainless steel tubes) were observed to be leaking small amounts of process fluid. Purifics stated that the source of the leaks were along the welds which connect a flow path between adjacent tubes in the racks (crossovers). Leaking was most likely caused by corrosion from heavy chloride concentrations encountered in previous tests for another client. The racks did not leak continuously. Purifics explained that the small holes eventually sealed up with a plug of TiO₂.

Purifics replaced the racks in the 4.8 kW demonstration Photo-Cat[®] unit with chloride resistant tubes. Tube material was not identified by Purifics but was described as a chloride resistant high moly tube.

5.3 CRU - Pulse system

In order to keep the ceramic filter from plugging with catalyst solids, the CRU is periodically (once per minute) pulsed with compressed air (approximately 80 psig for ¼ second duration). The back flow pulse created by the compressed air dislodges solids from the ceramic filter and allows them to flow to the Slurry Injection Pump. The air used in the pulse is discharged together with the treated solution through the piping that returns to batch tank. The addition of the pulse air to the batch tank causes vapors in the headspace to be discharged through the top vent of the batch tank. By designing the pulse air to have intimate contact with the treated liquid, there is stripping effect where volatile material can enter the vapor phase and discharge through the vent on the batch tank. To reduce emissions, it is suggested to design a hydraulic pulse system that uses a sealed diaphragm that does not inject air into the process.

6. TEST RESULTS & DISCUSSION

6.1 Liquid Characterization

The SAP (Sampling and Analysis Plan) specified analyses of the initial, intermediate and final composition of the liquid in the batch tank. Scheduled analyses are discussed in Section 4.3.1.1.

6.1.1 Feed (rinsate simulant solution)

The clean 1 m³ batch tank was charged with 300 L of tap water and allowed to circulate through the Photo-Cat[®] (with the lights off) for approximately 2 hours. The batch tank was sampled (Feed 1) via SP-1 to determine if any residual organic material was in the system or if any impurities were added with the tap water. Table 6-1 shows the results of the analyses performed on all grab samples from the batch tank (SP-1). The analyses reported that the circulated tap water had a TOC of 1.7 mg/L and a pH of 8.2. VOCs were reported which include acetone and acrolein at 170 and 110 ug/L respectively. Since the tap water was not initially sampled prior to being introduced into the Photo-Cat[®] batch tank, it is not definitive whether this low level of contaminants originated from the tap water or resided in the Photo-Cat[®] unit. However, acrolein is not normally detected in drinking water, and is not commonly found in surface water.⁹ This would suggest that the source of contaminants originated from the Photo-Cat[®] unit. This agrees with analyses performed on Feed-3,5,6,7,8 (Table 6-1) where apparently acrolein is generated as a by-product and then destroyed in the Photo-Cat[®] unit.

Instead of adding MEA directly to the batch tank, MEA (6.495 L) was added to a mixing jug along with warm tap water to total volume of 28 L. This solution was mixed well before adding its contents to the batch tank that already had 300 liters of tap water circulating. This created a total batch volume of 328 L of 2 wt% MEA solution. The simulated rinsate solution was then allowed to circulate through the Photo-Cat[®] system (with the lights off) for approximately 2 hours to ensure thorough mixing. At this point, a sample of the batch tank liquid (SP-1) was drawn and labeled Feed-2. The laboratory analysis of sample Feed-2 reported the TOC to be 8000 mg/L and the concentration of MEA to be 18,000 mg/L. This shows reasonable agreement with expected concentrations of 7865 mg/L TOC and 20,000 mg/L MEA.

After the Feed-2 sample, the pH of the simulant solution was measured and reported at 11.4. Purifics expected that ammonia would be produced from the destruction of MEA. In order to minimize the ammonia concentration in the headspace of the batch tank, the pH of the simulant solution was reduced to 7.0 with the addition of sulfuric acid. The solubility of ammonia in the simulant solution is expected to be greater at a pH of 7.0 than at 11.4.

At this point the simulant solution was ready for the validation test.

This document was prepared under contract with the United States Army for the sole purpose of evaluating the identified technology for potential application in the United States Army Chemical Demilitarization Program (CDP), based on information available to the reviewer at the time of the evaluation. Any opinions, findings, recommendations or conclusions expressed are stated in the context of the particular considerations of the CDP, and are not intended for use or reference in any way by any other party for any other purpose.

Table 6-1 Batch Tank Liquid Samples

Sample Location		SP-1	SP-1	SP-1	SP-1	SP-1	SP-1	SP-1	SP-1	SP-1	SP-1
Sample Description		Feed-1	Feed-2	Feed-3	Feed-4	Feed-5	Feed-6	Feed-7	Feed-8	Feed-9	Feed-10
Run Hour	Units	-4.50	0.00	9.83	21.33	29.33	44.33	52.00	68.67	76.75	92.33
Date of Sample		06/25/01	06/25/01	06/25/01	06/26/01	06/26/01	06/27/01	06/27/01	06/28/01	06/28/01	06/29/01
INORGANIC AND MISCELLANEOUS											
Aluminum	mg/L	<0.03	<0.03	NA	NA	NA	NA	0.32	NA	NA	0.26
Chromium	mg/L	<0.004	<0.004	NA	NA	NA	NA	0.13	NA	NA	0.019
Copper	mg/L	<0.006	<0.006	NA	NA	NA	NA	0.013	NA	NA	0.012
Iron	mg/L	<0.01	<0.075	NA	NA	NA	NA	3.5	NA	NA	0.088
Mercury	mg/L	<0.00005	<0.00005	NA	NA	NA	NA	<0.00005	NA	NA	0.00005
Titanium	mg/L	<0.01	<0.01	NA	NA	NA	0.3	0.29	NA	NA	<0.01
Zinc	mg/L	<0.01	<0.01	NA	NA	NA	NA	0.18	NA	NA	0.05
pH		8.19	11.36	2.41	2.2	2.2	2.43	2.7	4.63	4.26	3.64
TSS	mg/L	<2	6	23	20	<2	7	8	<2	<2	<2
COD	mg/L	<10	16000	14000	9700	6500	3100	1800	130	120	<10
TIC	mg/L	29	34	16	26	37	17	<10	<1.8	<1	<1
TOC	mg/L	1.7	8000	6900	5300	4100	1300	530	20	11	8.1
Ammonia	mg/L	9	52	710	1300	1700	2100	2000	2100	3600	3700
Organic Nitrogen (as N)	mg/L	4.3	5200	4200	3500	2900	2500	2500	2300	1300	1200
TKN (as N)	mg/L	13	5300	4900	4800	4600	4600	4500	4400	4900	4900
Cyanide	mg/L	<0.02	<0.02	0.13	0.059	0.019	<0.02	0.022	<0.02	<0.02	<0.02
Cyanates	mg/L	<0.5	<0.5	<10	<10	<10	<10	<10	<10	<10	<10
Thiocyanates	mg/L	<2	<2	<50	<50	<50	<50	<50	<50	<50	<50
Nitrate	mg/L	1.2	1.1	1.3	1.3	1.7	4.5	8.4	18	24	29
Nitrite	mg/L	0.36	<0.01	<0.011	<0.011	<0.01	<0.01	<0.01	<0.01	0.011	0.11
Sulfate	mg/L	30	27	14000	13000	13000	12000	13000	11000	13000	13000
Monoethanolamine	mg/L	<10	18000	9200	300	650	300	810	550	285	<100
Acetaldehyde	mg/L	0.01	0.03	1	1.2	1.4	<0.2	<0.33	<0.03	<0.03	<0.01
Formaldehyde	mg/L	<0.01	<0.01	0.79	0.57	0.52	0.93	0.53	0.13	0.07	0.06
Propanal	mg/L	<0.01	<0.01	<0.01	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Ethanol	mg/L	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
Methanol	mg/L	<5	<5	30	28	29	12	9	<5	<5	<5
1-Propanol	mg/L	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
2-Propanol	mg/L	<5	<5	<5	15	25	<5	<5	<5	<5	<5
MEK	mg/L	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Acetate	mg/L	<10	<10	820	2200	2300	830	260	<10	<10	<10
Butyrate	mg/L	<20	<50	<200	<200	<200	<20	<20	<20	<20	<20
Formate	mg/L	<5	<5	2600	2900	1300	170	44	<5	<5	<5
Propionate	mg/L	<15	<15	<150	<150	<150	<15	<15	<15	<15	<15
VOC - LIQUID											
Acetone	µg/L	170	190	7500	30000	26000	1700	490	180	<12.7	<12.7
Acrolein	µg/L	110	91	750	<1020	7500	240	360	220	<5.1	<5.1
Benzene	µg/L	<5	<5	<25	<100	<215	<10	<5	<5	<0.5	<0.5
Bromomethane	µg/L	<10	<10	<50	<200	<430	<20	12	<10	<1	1.1
2-Butanone	µg/L	<32	<32	200	<640	<1376	<64	<32	<32	<3.2	<3.2
Chloromethane	µg/L	<14	<14	<70	<280	<602	<28	17	<14	<1.4	<1.4
1,1-Dichloroethane	µg/L	<5	<5	<25	<100	<215	<10	<5	<5	<0.5	<0.5
Methylene Chloride	µg/L	<23	<23	<115	<460	<989	<46	30	<23	<2.3	<2.3
1,1,2,2-Tetrachloroethane	µg/L	<8	<8	<40	<160	<344	<16	<8	<8	<0.8	<0.8

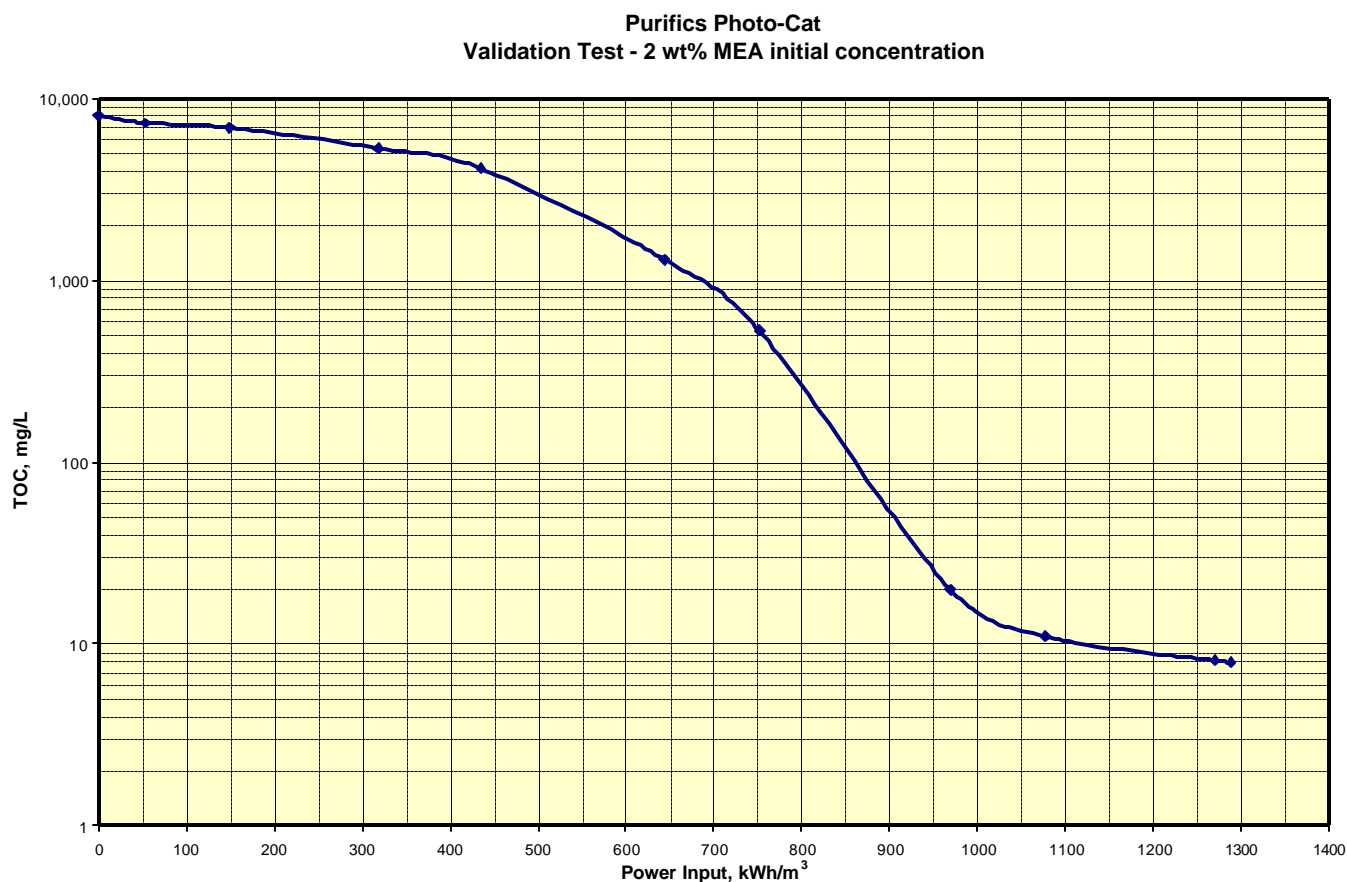
6.1.2 Intermediate and Final Liquid Samples

At 1130 hrs on June 25th, 2001, the validation test was commenced when the UV lights were turned on. Grab samples of the batch tank liquid were scheduled to be collected twice a day with the final sample (Feed 10) taken at 0750 hrs on June 29th, 2001. The analytical results are included in Table 6-1.

The initial organic loading was reported at 8000 mg/L TOC. This was followed by a steady decrease in TOC concentration as UV dosage accumulated with a final reported TOC concentration of 8.1 mg/L (99.9 wt% TOC destruction) (see Figure 6-1). Figure 6-2 illustrates trends of feeds and byproducts compared to the power input that is measured in kWh/m³ (the amount of UV lamp energy (in kWh) applied to 1 m³ of water). MEA concentration showed decreasing and increasing trends. This cannot be explained at this time but appears

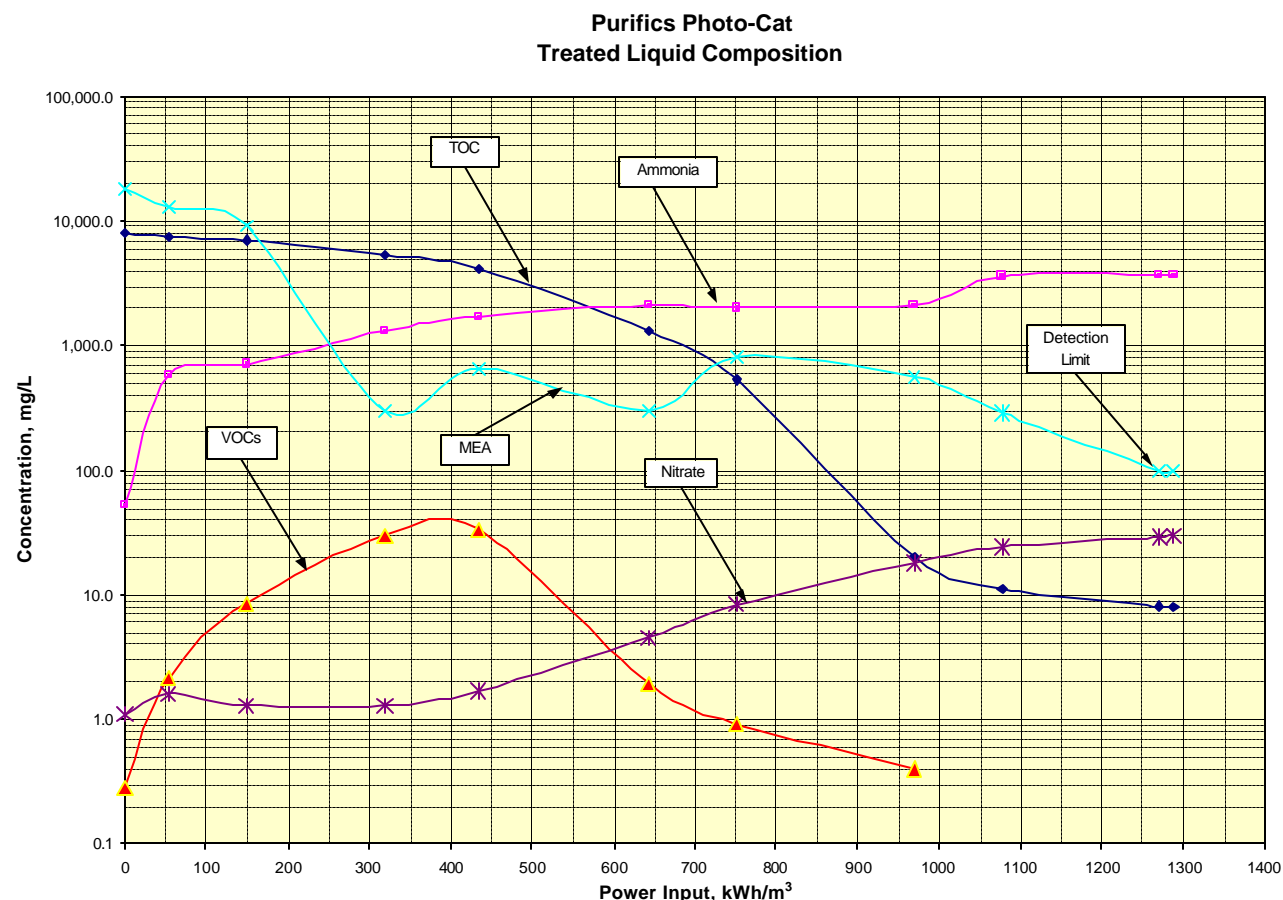
attributable to analytical error. The final MEA concentration was reported at less than 100 mg/L. Given the final TOC level of 8.1 mg/L in the final treated solution, there could be no more than 22 mg/L MEA (by calculation) in the final solution which would equate to a 99.9 wt% destruction efficiency.

Figure 6-1 Power Input vs. TOC



This document was prepared under contract with the United States Army for the sole purpose of evaluating the identified technology for potential application in the United States Army Chemical Demilitarization Program (CDP), based on information available to the reviewer at the time of the evaluation. Any opinions, findings, recommendations or conclusions expressed are stated in the context of the particular considerations of the CDP, and are not intended for use or reference in any way by any other party for any other purpose.

Figure 6-2 Treated Liquid Composition



By-products shown in Figure 6-2 from the processing of the rinsate simulant solution include ammonia, nitrates, and VOCs. Ammonia (equivalent to ammonia plus ammonium in the treated liquid), believed to be the major by-product of the process, had an initial concentration of 52 mg/L and steadily increased to a final concentration of 3700 mg/L. The amount of nitrogen in the ammonia produced represents nearly 73 wt% of the nitrogen content of the MEA that was destroyed. Nitrate concentration started at 1.2 mg/L and finished at 29 mg/L. Purifics believes that the low concentrations of nitrate ion are probably created by the oxidation of ammonia.¹⁰

VOCs reported in the treated solution include acetone and acrolein that were reported at 190 and 91 ug/L respectively in the initial simulant solution (Feed-2). Note that before the addition of MEA to the batch tank acetone and acrolein were reported at 170 and 110 ug/L (Feed-1) which suggest low levels of contamination were in the Photo-Cat[®] system prior to the validation test. As the UV dosage increased, the total VOCs detected increased to a peak of 33,500 ug/L of which approximately 78 wt% was acetone and approximately 22 wt% was acrolein. Following the peak, total VOCs concentrations decreased until

they fell below the analytical detection limits of the individual components. The final sample detected only a concentration of bromomethane at 1.1 ug/L.

Benzyl alcohol and di-n-butyl phthalate were the only SVOCs detected in the treated solution samples. Phthalates are used as plastisizers in the manufacturing of plastic pipe (such as PVC) and may have been leached from such materials in the Photo-Cat[®] demonstration system.

Samples of the solution in the batch tank were taken for metals analyses prior to MEA addition, after MEA addition, after 52 hours of UV dosage and after 92.3 hours of UV dosage (final treated solution). Metals, including aluminum, chromium, copper, iron, mercury, titanium, and zinc, were below detection limit for the initial 2 samples. At the 52 hour mark, the highest level of metals was detected, including some titanium. This could indicate that some of the catalyst (TiO₂) has passed through the Catalyst Recovery Unit (CRU) and into the batch tank. Each metal was detected at lower concentrations at the 92.3 hour mark when compared to the 52 hour mark. In addition, titanium was found below the analytical detection limit of 0.01 mg/L, which suggests the CRU was effectively recovering the TiO₂ catalyst. Nevertheless, the presence of metals in the treated solution suggests that some corrosion in the Photo-Cat[®] system is occurring.

As can be seen in Table 6-1 the concentration of sulfate in sample Feed-3 is reported at 14,000 mg/L. This reflects the addition of sulfuric acid to the system to bring the pH of rinsate simulant solution from 11.4 (after the addition of MEA) to 7.0.

Other by-products during the destruction process include the formation of simple carboxylic acids such as acetate and formate, which peaked at 2300, and 2900 mg/L respectively. The final analyses of the treated solution reported concentrations of acetate and formate to be below their respective detection limits which shows they are effectively destroyed.

6.1.3 Final Treated Liquid Disposal Evaluation

Based on the Engineering Scale Test (EST) results, liquid waste generated by a Photo-Cat[®] system treating a MEA based solution (simulating a NSCMP rinsate solution) should not normally be regulated as a hazardous waste and should typically require minimal, if any, pretreatment before it could be discharged to a wastewater treatment facility. This statement is supported by the fact that there are currently no specific Destruction and Removal Efficiencies (DRE) criteria under RCRA that would apply to the Photo-Cat[®] technology. Chemical treatment in general and the Photo-Cat[®] technology specifically would be subject to Subpart X – Miscellaneous Units. Under Subpart X, treatment standards (DRE) are established on a case-by-case basis within the permitting process. The endpoint would be resulting effluent that was non-hazardous or otherwise acceptable for discharge.

In addition, there are some “Derived-from” considerations that need to be investigated. Hazardous waste regulation of the Photo-Cat[®] effluent due to the “derived-from” rule would only be a potential issue in a limited number of states because the EPA and most states have not listed agent or agent-derived

This document was prepared under contract with the United States Army for the sole purpose of evaluating the identified technology for potential application in the United States Army Chemical Demilitarization Program (CDP), based on information available to the reviewer at the time of the evaluation. Any opinions, findings, recommendations or conclusions expressed are stated in the context of the particular considerations of the CDP, and are not intended for use or reference in any way by any other party for any other purpose.

wastes as listed hazardous wastes. While many states with stockpile locations (e.g., Maryland, Colorado, Utah, Oregon) have elected to list these wastes as hazardous waste, Arkansas has not. Even where listed, a Purifics unit treating NSCMP wastes would have to be operated under a RCRA Permit (under Subpart X). Typically the endpoint of the treatment process required by permit would be a non-hazardous effluent acceptable for discharge or other treatment. Effluent meeting the standards of the permit would no longer be regulated as a hazardous waste. If a regulatory agency were to take these interpretations to an extreme and determine that the Photo-Cat[®] effluent was still a listed hazardous waste based on the derived-from rule, it could still be possible to "delist" the effluent by submitting a demonstration that the resulting waste stream no longer contained hazardous levels of hazardous constituents.

It is expected that wastewater from a Photo-Cat[®] treatment system or any rinsate post-treatment technology would be discharged to a wastewater treatment facility before ultimate disposal. A primary evaluation criteria for determining the viability of disposing of liquid waste generated during operation of the Photo-Cat[®] system is a limit of 25 ppm (25 mg/L) on Total Organic Carbon (TOC). This value is based on the existing TOC concentration permitted in wastewater discharged from the Pine Bluff Arsenal Central Waste Treatment facility to the Arkansas River, and is therefore a conservative evaluation criteria. TOC measured in the final sample from the NSCMP rinsate simulant test run was 8.1 mg/L, well below the 25 ppm target criteria for acceptable discharge. Other measures of organic loading (e.g., COD, MEA, VOC) were similarly reduced from their initial elevated concentrations to low levels.

pH of the final wastewater was measured as 3.64. Discharge pH requirements can vary with location based on local wastewater treatment facility influent characteristics, or receiving water conditions, but typically require a range of 6.0 – 9.0. Thus, pH adjustment of the final system effluent would be necessary prior to discharge to a local wastewater treatment facility or a direct surface water discharge.

All of the metal concentrations analyzed were below ppm levels, less than limits typical for most discharges to sewer systems. Concentrations of nitrogen-bearing MEA breakdown products (ammonia, organic nitrogen, nitrates) and sulfate were elevated to levels that could potentially require additional pretreatment or off-site disposal depending upon site-specific receiving stream conditions. Even for sewer discharge, acceptability would depend on the stringency of effluent limits imposed on the receiving wastewater treatment facility and that facility's capability to remove ammonia and/or nitrogen compounds. In addition, sulfate is present in the discharge only due to process pH adjustment (using sulfuric acid) which resulted in a concentration of 14,000 ppm in the treated liquid and may not be an issue for disposal if other acids (such as nitric acid) are used for pH adjustment.

6.2 Headspace Characterization

6.2.1 Batch Tank Headspace Analysis

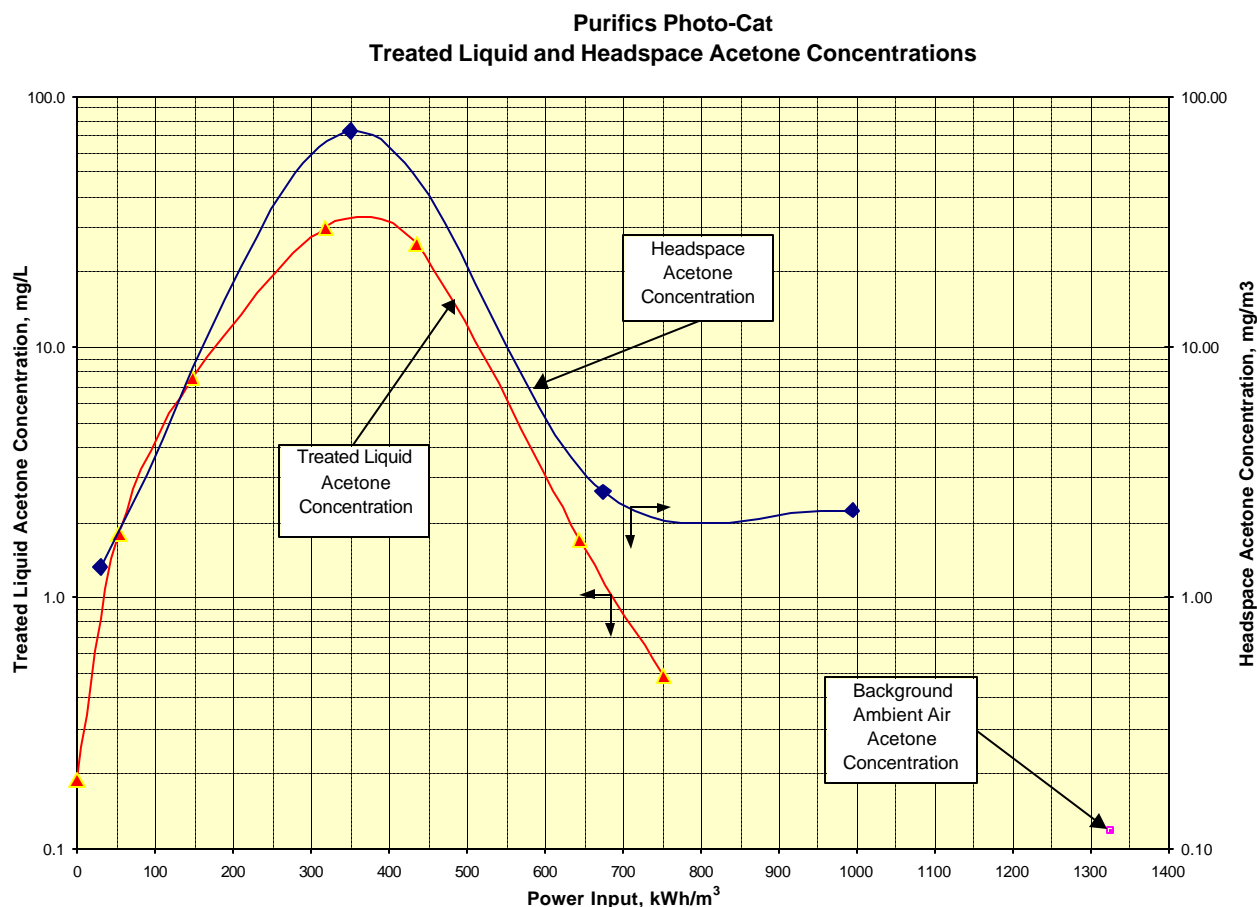
The analyses of the headspace of the batch tank are summarized in Table 6-2. The initial headspace analyses which was sampled in the first 4 hours of the validation test, reported a total VOC (detected) concentration of 3504 ug/m³ of which acetone, dichloromethane, and meta and para xylenes were the major components (> 75% of total VOCs). Subsequent samples showed the total VOCs increased to 72,900 ug/m³ and subsequently leveled off at approximately 2900 ug/m³. Again, the majority (> 99%) of total VOCs were due to acetone concentrations that were also detected in the treated liquid solution as discussed in Section 6.1.2. Figure 6-3 shows the relationship between acetone concentration in the treated liquid solution and acetone in the headspace.

Table 6-2 Headspace Analyses

Sample Location		SP-03	SP-03	SP-03	SP-03	SP-7
Sample Description		Headspace	Headspace	Headspace	Headspace	Background
Run Hour ³	Units	2.00	23.42	46.42	70.50	Air
06/25/2001 11:30		13:30	10:55	9:55	10:00	10:00
Date of Sample		06/25/01	06/26/01	06/27/01	06/28/01	06/29/01
VOC - GAS						
Acetone	µg/m ³	1329	72479	2658	2223	118
Benzene	µg/m ³	68	21	<32	<6.5	<16
Bromomethane	µg/m ³	<30	<30	<59	<12	<30
2-Butanone (MEK)	µg/m ³	<570	<570	<1140	<228	<570
Chloromethane	µg/m ³	<11	<11	<21	<4.2	<11
1,1-Dichloroethane	µg/m ³	78	<21	<41	<8.2	<21
Dichlorodifluoromethane	µg/m ³	<25	<25	<50	<10	44
Dichloromethane	µg/m ³	601	216	230	671	67
Ethylbenzene	µg/m ³	203	<22	<44	<8.8	<22
2-Propanol	µg/m ³	<188	<188	<375	<75	95
1,1,2,2-Tetrachloroethane	µg/m ³	<35	50	<70	<14	<35
Tetrachloroethene	µg/m ³	<34	39	<69	<14	<34
1,1,1-Trichloroethane	µg/m ³	61	47	<83	<17	<42
Trichloroethene	µg/m ³	115	<41	<82	<16	<41
1,1,2-Trichloro-1,2,2-trifluoroethane	µg/m ³	94	<39	<78	86	72
Toluene	µg/m ³	54	20	<38	10	20
o-Xylene	µg/m ³	194	<22	<44	<8.8	<22
m&p-Xylenes	µg/m ³	707	<33	<66	<13	<33
Total	µg/m ³	3504	72872	2888	2990	416
SVOC - GAS						
Benzyl alcohol	µg/dscf	<0.40	<0.39	<0.40	<0.39	
Benzyl butyl phthalate	µg/dscf	<0.12	<0.12	<0.12	0.15	
Bis(2-ethylhexyl)phthalate	µg/dscf	<0.28	<0.27	<0.28	<0.27	
Di-n-butyl phthalate	µg/dscf	<0.22	<0.21	<0.22	<0.22	
Naphthalene	µg/dscf	0.08	<0.06	<0.06	<0.06	
MISC - GAS						
HCN	µg/dscf	0.56	6.98	11.73	1.56	
Ammonium	µg/dscf	5.75	0.78	2.25	4.96	
Monoethanolamine	µg/dscf	<4.08	<3.90	<3.82	<3.81	
Oxides of Nitrogen (NOx, as NO2)	µg/dscf	24.74	16.87	28.90	21.10	
O ₂	%	21.90	9.40	17.40	26.20	21.8
CO ₂	%	2.20	17.00	27.10	3.00	0.1
N ₂	%	77.80	75.50	57.10	72.60	79.3
H ₂	%	<0.10	<0.10	<0.10	<0.10	<0.10
CO	%	<0.10	0.50	<0.10	<0.10	<0.10
THC (methane)	ppm	73.80	118.00	22.00	6.10	6.1

Notes:

- (1) NA = Sample not taken or sample not analyzed.
 < = Undetected at detection limit.
- (2) Shaded areas represent components undetected at the analytical detection limit.

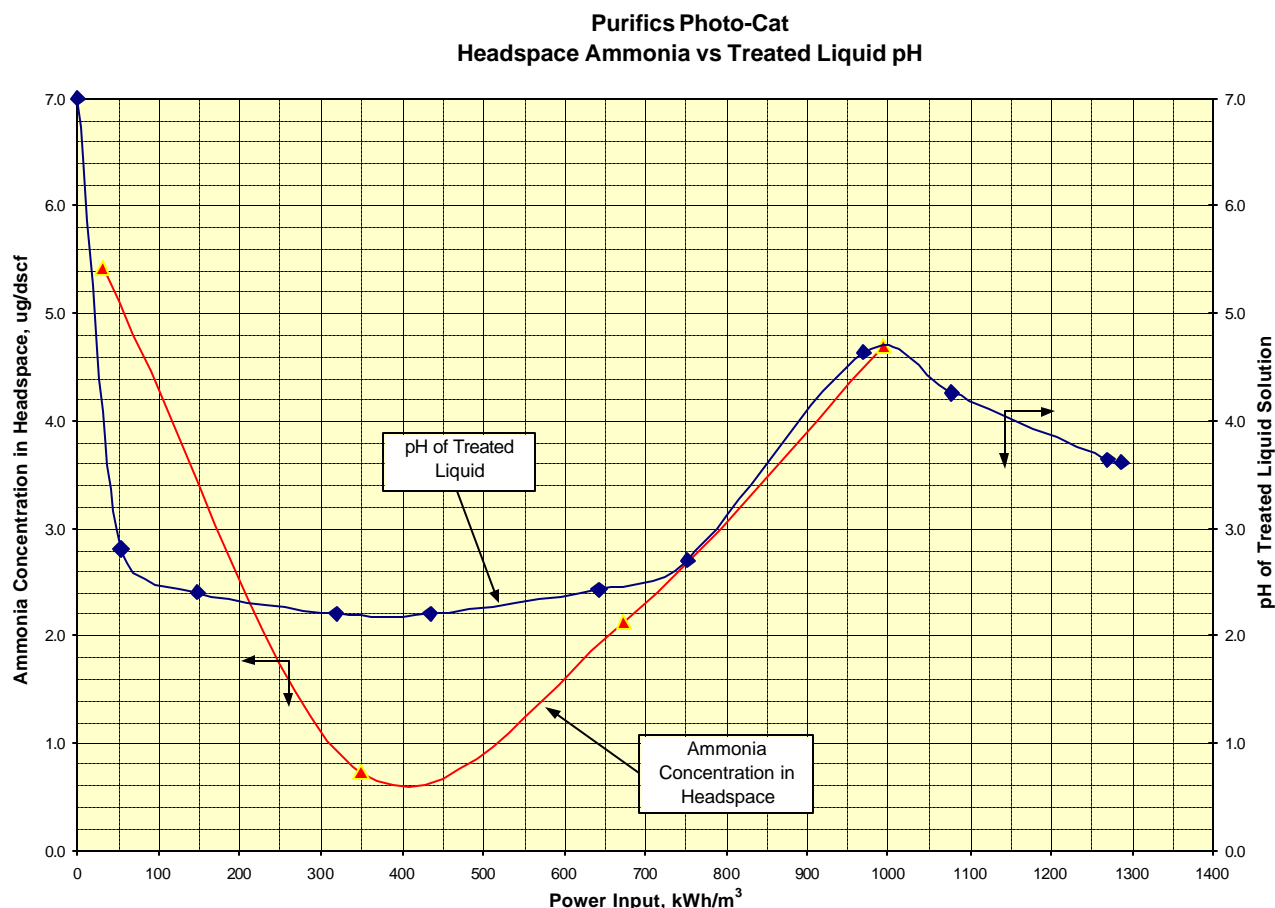
Figure 6-3 Acetone Concentrations

In addition to dichloromethane other halogenated components including 1,1-dichloroethane, 1,1,1-trichloroethane, trichloroethene, and 1,1,2-trichloro-1,2,2-trifluoroethane were detected. The background air sample also showed some halogenated compounds including dichlorodifluoromethane, dichloromethane and 1,1,2-trichloro-1,2,2-trifluoroethane. Since there were no intentional chlorinated or fluorinated compounds added to the Photo-Cat[®] unit, the reason for their presence in the analyses is unknown. Sources of chlorides or fluorides could enter the Photo-Cat[®] system from the surrounding ambient air via the compressed air system (through the pulse system) or in breathing of the batch tank which occurred during sampling activities. Another, more likely source includes residual contamination from demonstration runs performed prior to this test campaign which used highly chlorinated feeds.

No significant concentrations of SVOCs were reported in the analyses. HCN was detected throughout the validation test and ranged from 0.56 to 11.73 ug/dscf. Ammonia, which is measured as ammonium in the gas sampling train, ranges from 5.4 ug/dscf (NH₃) to 0.74 ug/dscf (NH₃). The pattern of ammonia in the headspace suggests that pH of the treated liquid had an effect on the

concentration of ammonia released to the headspace as can be seen in the Figure 6-4.

Figure 6-4 Headspace Ammonia vs. Treated Liquid pH



The CO₂ concentrations (Table 6-2) in the headspace give important indications of the destruction of MEA and by-products. CO₂ begins at a low concentration (2.2 vol%) and peaks at 27 vol% and subsequently falls off to 3 vol% at the end of the treatment duration. This trend indicates the conversion of organic material to CO₂. At the end of the treatment process, nearly all of the conversion of organic material has been completed and is reflected by the lower CO₂ concentrations in the headspace.

6.2.2 Air Emissions

Emission standards applicable to a specific unit will be a function of the unit's location and size as determined in a case-by-case control technology evaluation under Prevention of Significant Deterioration (PSD), Non-attainment New Source Review, or a state minor source construction permit program. These programs, and subsequent control technology determinations, are triggered based on a source's annual "potential to emit" on a mass emissions

basis. Air emissions from NSCMP rinsate simulant processing in the Photo-Cat[®] system are limited to that vented from the process feed tank as the waste stream is recirculated through the treatment system. The vapor space in the storage tank is not mechanically ventilated, and instead vents limited quantities of gas primarily from gas evolution during the treatment process (CO₂, CRU pulse air along with vaporized by-products). Because these flow rates were minimal (estimated at less than 4 L/min) the associated mass emissions of potential air pollutants are expected to be very low, well below thresholds triggering these permit and control technology requirements.

In some cases, control technology requirements are established for specific classes of sources based on technology or industry classifications under Federal New Source Performance Standards (NSPS), National Emissions Standards for Hazardous Air Pollutants (NESHAPs) or pertinent state/local source category standards. Currently, no NSPS or NESHAPs have been established that would apply directly to the Photo-Cat[®] technology. Although not directly applicable, the wastewater provisions of the NESHAP for the Synthetic Organic Chemical Manufacturing Industry (SOCMI) (40 CFR 63, Subpart G) could be used as a comparative benchmark for the Photo-Cat[®] process vent emissions. These standards typically require VOC emissions vented from sources of this type to be below 500 ppm. VOC emissions monitored as THC during the NSCMP rinsate simulant processing peaked at 118 ppm on the second day of processing, and declined to a final level of 6.1 ppm, all well below the Subpart G standard.

Because the unit is actually vented to the workplace (rather than directly to ambient outdoor air), Occupational Safety and Health Administration (OSHA) workplace exposure standards are also pertinent benchmarks for comparison. MEA in the vapor was undetected in all samples and was thus below the OSHA 8-hour exposure standard of 3 ppm (6 mg/m³). Hydrogen cyanide (HCN), also regulated by EPA as a hazardous air pollutant (HAP), and ammonia (NH₃) appeared to be generated during processing and detected in the vapor space. However, the maximum concentration measured of each compound was two orders of magnitude below their respective standards [10 ppm (11 mg/m³) HCN; 50 ppm (35 mg/m³) NH₃]. Locating the vent outdoors or other simple control techniques (e.g., conservation vent) would further minimize potential air emissions/exposure issues.

6.3 TiO₂ Slurry Analyses

Table 6-3 is a summary of the analyses performed on the TiO₂ slurry that consists of the circulated treated solution and the TiO₂ catalyst (solid particles). The results are similar to the results shown for the intermediate and final liquid samples in Section 6.1.2. No build-up of components or unusual concentrations were detected. The results indicate that the water in the slurry circulation system was treated to the same extent as the bulk treated solution.

This document was prepared under contract with the United States Army for the sole purpose of evaluating the identified technology for potential application in the United States Army Chemical Demilitarization Program (CDP), based on information available to the reviewer at the time of the evaluation. Any opinions, findings, recommendations or conclusions expressed are stated in the context of the particular considerations of the CDP, and are not intended for use or reference in any way by any other party for any other purpose.

Table 6-3 TiO₂ Slurry Analyses

Sample Location		SP-6	SP-6
Sample Description		Slurry-1	Slurry-2
Run Hour		3.50	92.50
	06/25/2001 11:30	15:00	8:00
Date of Sample		06/25/01	06/29/01
INORGANIC AND MISCELLANEOUS			
Aluminum	mg/L	<0.3	0.29
Chromium	mg/L	0.056	0.063
Copper	mg/L	<0.06	0.012
Iron	mg/L	2.9	1.1
Mercury	mg/L	<0.00005	0.00006
Titanium	mg/L	2.1	0.64
Zinc	mg/L	0.15	0.061
pH	mg/L	2.81	3.61
TSS	mg/L	190	44
COD	mg/L	14000	71
TIC	mg/L	12	<1
TOC	mg/L	7300	7.9
Ammonia	mg/L	570	3700
Organic Nitrogen (as N)	mg/L	4700	1000
TKN (as N)	mg/L	5200	4800
Cyanide	mg/L	0.39	<0.02
Cyanates	mg/L	<10	<10
Thiocyanates	mg/L	<50	<50
Nitrate	mg/L	1.6	30
Nitrite	mg/L	<0.011	<0.01
Sulfate	mg/L	14000	13000
Monoethanolamine	mg/L	13000	<100
Acetaldehyde	mg/L	1	<0.01
Formaldehyde	mg/L	0.59	0.08
Propanal	mg/L	<0.01	<0.01
Ethanol	mg/L	<5	<5
Methanol	mg/L	27	<5
1-Propanol	mg/L	<5	<5
2-Propanol	mg/L	<5	<5
MEK	mg/L	<0.01	<0.01
Acetate	mg/L	320	<10
Butyrate	mg/L	<200	<20
Formate	mg/L	480	<5
Propionate	mg/L	<150	<15
VOC - LIQUID			
Acetone	µg/L	1800	<12.7
Acrolein	µg/L	240	<5.1
Benzene	µg/L	<5	<0.5
Bromomethane	µg/L	<10	<1
2-Butanone	µg/L	100	<3.2
Total	µg/L	2140	0
SVOC - LIQUID			
Benzyl alcohol	µg/L	<2	<2
Benzyl butyl phthalate	µg/L	<0.6	<0.6
Bis(2-ethylhexyl)phthalate	µg/L	1.6	<1.4
Di-n-butyl phthalate	µg/L	<1.1	<1.1
Naphthalene	µg/L	<0.3	<0.3
Total	µg/L	1.6	0

Notes:

- (1) NA = Sample not taken or sample not analyzed.
 < = Undetected at detection limit.
 (2) Shaded areas represent components undetected at the analytical detection limit.

6.4 Material Balance

One of the objectives of the EST of the Photo-Cat[®] Process was to determine an overall material balance. To accomplish this objective, the Test Plan required collection of sufficient data to complete an overall material balance. Table 6-4 shows an estimate of the overall material balance and select component balances. The overall material balance accounts for nearly 96 wt% of the feed materials. The apparent loss of 4 wt% is attributed to moisture lost in the venting of the batch tank, CO₂ and ammonia in the off-gas, and leakage.

Table 6-4 Material Balance

Stream Definition	Initial Simulant Feed	Peroxide Added	Samples Removed from System	Emissions from Batch Tank	Final Treated Solution	Mass Balance Check (In-Out)	Destruction Efficiency
	[kg]	[kg]	[kg]	[kg]	[kg]	[kg]	
Water	320.4	49.1	46.1	-	341.8	-18.4	
MEA	6.531	-	0.198	-	0.007	6.3	99.89%
H ₂ O ₂	-	26.42	-	-	-	26.4	
TOC	2.624	-	0.154	-	0.003	2.5	99.89%
TKN ¹ (as N)	1.738	-	0.243	-	1.676	-0.2	
TOTAL	331.3	75.48	46.70	-	343.5	16.6	

Notes:

(1) TKN is Total Kjeldahl Nitrogen which is the sum of organic nitrogen and ammonia.

6.4.1.1 Elemental Material balances for N

One of the objectives of the EST of the Photo-Cat[®] process was to determine the fate of relevant components in the system. The component of interest was Nitrogen. To accomplish this objective, the Test Plan required collection of sufficient data to complete a material balance for these components. Based on analyses from the laboratory, 87 wt% of the nitrogen feed to the system (MEA) is accounted for in the final treated solution. This indicates that most of the amino groups in the MEA form ammonia upon MEA destruction.

6.5 NSCMP Implementation

Based upon the results of this test, the Photo-Cat system required 960 kWh/m³ of treatment to reduce the TOC of a 2% MEA solution (initial TOC = 8000 ppm) below 25 ppm TOC. Based upon the volume reduction from sampling and the associated TOC load removed from sampling activities, Purifics conservatively estimated that for a full-scale application (120 gpd of 2 wt% MEA rinsate) approximately 1100 kWh/m³ of treatment would be required.

The required treatment levels are directly proportional to the mass loading of the MEA. Based on the demonstrated level of Photo-Cat performance, the Photo-Cat can

This document was prepared under contract with the United States Army for the sole purpose of evaluating the identified technology for potential application in the United States Army Chemical Demilitarization Program (CDP), based on information available to the reviewer at the time of the evaluation. Any opinions, findings, recommendations or conclusions expressed are stated in the context of the particular considerations of the CDP, and are not intended for use or reference in any way by any other party for any other purpose.

mineralize rinsate MEA solutions below 25 ppm at a rate of 20g of MEA per kWh of photocatalytic treatment. This ratio will be used to determine:

- The design full-scale Photo-Cat power requirement to treat existing rinsate solutions in a reasonable time frame.
- The required batch processing time for each batch of rinsate batches.

Assuming a full-scale system would treat approximately 120 gallons per day (based on rinsate generated from the neutralization of eight 4.2" mortars) of 2% MEA rinsate, a 21 kW Photo-Cat system is required for destruction below 25 ppm TOC. The footprint of this system would be 4' X 11' by 5' tall.

7. CONCLUSIONS

Test data and observations from two Work-up Runs and one Validation test were completed as part of the Engineering Scale Testing of the Photo-Cat[®] process and were evaluated in accordance with the test criteria. Test conclusions are summarized below for each listed objective.

1. Demonstrate stable operability at maximum continuous throughput.

- Continuous stable operation of the Photo-Cat[®] unit showed destruction of greater than 99 wt% MEA in the 2 wt% MEA rinsate simulant solution feed. In addition, it was shown that the Photo-Cat[®] unit consistently produced a final treated solution, which had less than 25 ppm TOC. In fact, the final treated solution had a TOC of 8 ppm, which represents a destruction of greater than 99 wt%.
- The 4.8 kW Photo-Cat[®] unit destroyed 328 liters of 2 wt% MEA rinsate simulant in 92.3 hours of treatment.
- Final treated liquid generated by the Photo-Cat[®] unit (treating a 2 wt% MEA rinsate simulant) should not normally be regulated as a hazardous waste and should typically require minimal, if any, pretreatment before it could be discharged to a federal wastewater treatment facility.
- Air emissions during the treatment of a 2 wt% MEA rinsate simulant from the Photo-Cat[®] system are limited to that vented from the process feed tank as the waste stream is recirculated through the treatment system. The vapor space in the storage tank is not mechanically ventilated, and instead vents limited quantities of gas primarily from gas evolution during the treatment process (CO₂, filter pulse air along with vaporized by-products). Because these flow rates were minimal (estimated at less than 4 L/min) the associated mass emissions of potential air pollutants are expected to be very low, well below thresholds triggering these permit and control technology requirements.
- No physically solid wastes were discovered in Photo-Cat[®] system during the treatment of a 2 wt% MEA rinsate simulant.

2. Demonstrate the fate of Nitrogen contained in the feed material.

- The overall material balance indicated reasonable accountability and that nearly all organic nitrogen (amine group of MEA) was converted to ammonia/ammonium which remained in the final treated liquid.

3. Provide basic engineering data to evaluate practicality for implementation in NSCMP.

- The existing mobile 4.8 kW unit should be capable of 27 gallons of rinsate per day. A 21 kW Photo-Cat[®] Unit (4'x11'x5' tall) should be capable of processing 120 gallons of 2 wt% MEA rinsate per day. Since Purifics has sold Photo-Cat units on the order of 100 kW, the proposed 21 kW unit is clearly within the practical design range.

4. Quantify and document key operating and engineering design parameters.

- The Photo-Cat[®] is a low temperature (45°C as tested) low pressure (< 50 psig) process that showed good reliability, maintainability, and operating characteristics.
- Key operating parameters including an estimated treatment rate of 960 kWhr/m³ to process 2 wt% MEA rinsate simulant to a final TOC of 25 ppm, and stoichiometric dosages of hydrogen peroxide dosage were quantified during the EST. These parameters enable the core-technology to be easily scaled for NSCMP requirements.

This document was prepared under contract with the United States Army for the sole purpose of evaluating the identified technology for potential application in the United States Army Chemical Demilitarization Program (CDP), based on information available to the reviewer at the time of the evaluation. Any opinions, findings, recommendations or conclusions expressed are stated in the context of the particular considerations of the CDP, and are not intended for use or reference in any way by any other party for any other purpose.

8. RECOMMENDATIONS

Based on these conclusions, it is recommended that further testing be conducted to demonstrate component destruction of actual NSCMP rinsate. The following objectives should be included in future testing:

- Characterization of final treated rinsate solution.
- Quantification of key engineering scale-up parameters such as treatment level and hydrogen peroxide dosage.
- Destruction efficiency of schedule 2 compounds.
- Characterization of gaseous emissions from the process.
- Determine sampling and analyses methods to improve on the characterization of difficult to analyze materials such as MEA.
- Applicability to other NSCMP feeds.
- Material balances – overall and for key elements.

9. ACRONYMS & ABBREVIATIONS

ACRONYMS & ABBREVAITIONS

DEFINITIONS

316 SS	316 Stainless Steel
ACWA	Assembled Chemical Weapons Assessment
ATAP	Alternative Technologies and Approaches Program
COC	Chain-of-Custody
COD	Chemical Oxygen Demand
CRU	Catalyst Recovery Unit
CWM	Chemical Warfare Materiel
EST	Engineering Scale Testing
GB	Chemical agent, Nerve agent, Sarin
GPD	Gallons per day
HAP	Hazardous Air Pollutants
HD	Chemical agent, Sulfur Mustard (distilled)
KW	kilowatts
KWh/m ³	Kilowatt-hour per cubic meter
L/min	Liters per minute
MEA	Monoethanolamine
MMD	Munitions Management Device
NESHAP	National Emission Standards for Hazardous Air Pollutants
NSCMP	Non-Stockpile Chemical Materiel Program
NSPS	New Source Performance Standards
ORP	Overarching Research Plan
PLC	Program Logic Controller
PMCD	Program Manager for Chemical Demilitarization
ppm	Parts per million
ppm _{v,d}	Parts per million by volume – dry basis
PSD	Prevention of Significant Deterioration
PVC	Polyvinyl chloride
RACT	Reasonably Available Control Technology
RCRA	Resource Conservation and Recovery Act
SAP	Sampling and Analysis Plan
SCADA	Supervisory Control and Data Acquisition
SVOC	Semi-volatile organic compound
THC	Total Hydrocarbon
TIC	Total Inorganic Carbon
TKN	Total Kjeldahl Nitrogen
TOC	Total Organic Carbon
TON	Total Organic Nitrogen
TOX	Total Chlorinated Organic Compound
TRC	TRC Environmental Corporation

This document was prepared under contract with the United States Army for the sole purpose of evaluating the identified technology for potential application in the United States Army Chemical Demilitarization Program (CDP), based on information available to the reviewer at the time of the evaluation. Any opinions, findings, recommendations or conclusions expressed are stated in the context of the particular considerations of the CDP, and are not intended for use or reference in any way by any other party for any other purpose.

**ACRONYMS &
ABBREVAITONS**

TSS

UV/Ox

VOC

DEFINITIONS

Total Suspended Solids

Ultraviolet Oxidation

Volatile Organic Compound

This document was prepared under contract with the United States Army for the sole purpose of evaluating the identified technology for potential application in the United States Army Chemical Demilitarization Program (CDP), based on information available to the reviewer at the time of the evaluation. Any opinions, findings, recommendations or conclusions expressed are stated in the context of the particular considerations of the CDP, and are not intended for use or reference in any way by any other party for any other purpose.

10. REFERENCES

- ¹ Contaminants treated with Photo-Cat[®] Systems, <http://www.purifics.com/treat.html>.
- ² "Purification of Heavy Water of Organic Contaminates Using Photo-Cat[®]", Tony Powell, Brian Butters and Colin Barfoot, Purifics[®], Feb. 1996, Revised May 1997.
- ³ Powell, Tony, "Final Report and Answers to Questions", email to Steven Burnham, 9/29/01.
- ⁴ Foster Wheeler Environmental, Department of the Army, Shell Oil Company, U.S. Fish and Wildlife Service, "Rocky Mountain Arsenal, M139 Bomblets, Destruction Completion Report", July 10, 2001.
- ⁵ Utah Division of Solid and Hazardous Waste, "MMD-1, Research Development and Demonstration RCRA Permit", Issued May 14, 1999, Appendix 4A.
- ⁶ Purifics Environmental Technologies, Inc., "Draft – Photo-Cat[®] Test Report, Destruction of Rinsate Simulant Solution", Sept. 5, 2001, p. 3.
- ⁷ Purifics Environmental Technologies, Inc., "Draft – Photo-Cat[®] Test Report, Destruction of Rinsate Simulant Solution", Sept. 5, 2001, p. 4.
- ⁸ Purifics Environmental Technologies, Inc., "Draft – Photo-Cat[®] Test Report, Destruction of Rinsate Simulant Solution", Sept. 5, 2001, p. 5.
- ⁹ Agency for Toxic Substances and Disease Registry (ATSDR). *Toxicological Profile for Acrolein*. U.S. Public Health Service, U.S. Department of Health and Human Services, Atlanta, GA. 1989.
- ¹⁰ Purifics Environmental Technologies, Inc., "Draft – Photo-Cat[®] Test Report, Destruction of Rinsate Simulant Solution", Sept. 5, 2001, p. 6.

